REGISTERED NO. M. 3121

PROCEEDINGS

OF THE

INDIAN ACADEMY

OF SCIENCES

VOL. XII] *SECTION A* [NO. 4

OCTOBER, 1940

Price Rs. 2 or 3 Sh. *Annual Subscription Rs. 18*

PRINTED AT THE BANGALORE PRESS, BANGALORE CITY, BY G. SRINIVASA RAO, SUPERINTENDENT, AND PUBLISHED BY THE INDIAN ACADEMY OF SCIENCES, HEBBAL, BANGALORE.

EFFECT OF TEMPERATURE ON THE ULTRASONIC VELOCITY IN LIQUIDS

By V. Suryaprakasam

(From the Department of Physics, Andhra University, Waltair)

Received September 3, 1940

(Communicated by Prof. S. Bhagavantam)

1. *Introduction*

A considerable amount of work, relating to the determination of the sound velocities in and the adiabatic compressibilities of liquids, has been done in recent years. Comprehensive references to literature are to be found in Bergmann's book on 'Ultrasonics and Their Scientific and Technical Applications'. Extensive data with regard to the variation of the adiabatic compressibility of liquids with temperature are, however, not available. Tyrer[1] has done some work in this direction. He used a piezometer and determined the compressibility in the range 0° C. to 80° C. for a few liquids. Freyer, Hubbard and Andrews[2] used a sonic interferometer for the same purpose and studied the variation of the adiabatic compressibility of some common liquids in the range 0° C. to 50° C. Methods based on the diffraction of light by ultrasonic waves have, however, come to be used extensively by the recent investigators. Amongst these, mention may be made of Bhagavantam and Joga Rao[3] who studied the dependence on temperature of the adiabatic compressibility in some highly viscous liquids such as glycerine. In the present paper, the author has extended these investigations to eleven organic liquids. Data at some of the temperatures are available, from the earlier work of Tyrer and Freyer, Hubbard and Andrews, for only three of the eleven liquids chosen in this investigation. In the remaining eight liquids, the dependence of the ultrasonic velocity on temperature has been studied here for the first time.

2. *Experimental Details*

A single valve (D. 0·24 Mullard) in a Hartley type of circuit is used for generating the oscillations. A quartz crystal, the thickness of which is

[1] *Jour. Chem. Soc.*, 1914, **105**, 2534.

[2] *Jour. Amer. Chem. Soc.*, 1929, **51**, 759.

[3] *Proc. Ind. Acad. Sci.*, 1939, **9**, 312.

about 2 mm., sets up the ultrasonic waves in the liquid. The fundamental frequency of the crystal is about 1·6 megacycles. λ 5460 A.U. of the mercury arc is used as the source of light. The optical arrangement adopted is slightly different from the conventional one and has been evolved here with a view to bring the determination of the ultrasonic velocity in a liquid within the purview of the routine experiments usually performed in an Honours Laboratory. The cell containing the liquid is mounted on the prism table of a well-adjusted spectrometer and the crystal is so held in the liquid that the ultrasonic waves are generated in a vertical plane, the direction of propagation being horizontal and perpendicular to the axis of the collimator. In such an arrangement, the collimator of the spectrometer serves to collimate the light and the diffraction pattern is observed through the telescope attached to the spectrometer itself. The angle of diffraction is directly measured on the prism table as in an ordinary grating experiment with an accuracy of about one-half per cent. These arrangements have been adopted throughout the present investigation. A Philips heterodyne wavemeter, capable of measuring frequencies correct to 0·2 per cent. has been used for measuring the frequencies. Such measurements are made for each liquid separately and also at each one of the temperatures employed. The variation in the frequency with temperature has been found to be small between 30° C. and 120° C. Throughout the investigation, the crystal has been made to oscillate with a frequency of about 7·2 m.c. corresponding to its fifth harmonic. The desired temperature increase is effected gradually by keeping the container cell at the centre of a wide cylindrical electric heater made specially for the purpose. The density of the liquid, at each one of the temperatures employed, has also been determined with an ordinary pyknometer for all the liquids. The adiabatic compressibilities are then calculated in the usual manner.

All the liquids used, except bromobenzene and propyl alcohol, have been carefully distilled at constant boiling points. The latter are taken from freshly opened bottles.

3. Results

Results of measurements with the eleven liquids studied are tabulated in Tables I to XI. Tyrer's results for three of the liquids are given in Tables I, II and III along with those of the author for comparison. In the same Tables, data for three temperatures only are given in brackets below the corresponding figures obtained by the author. These are due to Freyer, Hubbard and Andrews. In the accompanying chart, temperature variations of the ultrasonic velocity are represented graphically.

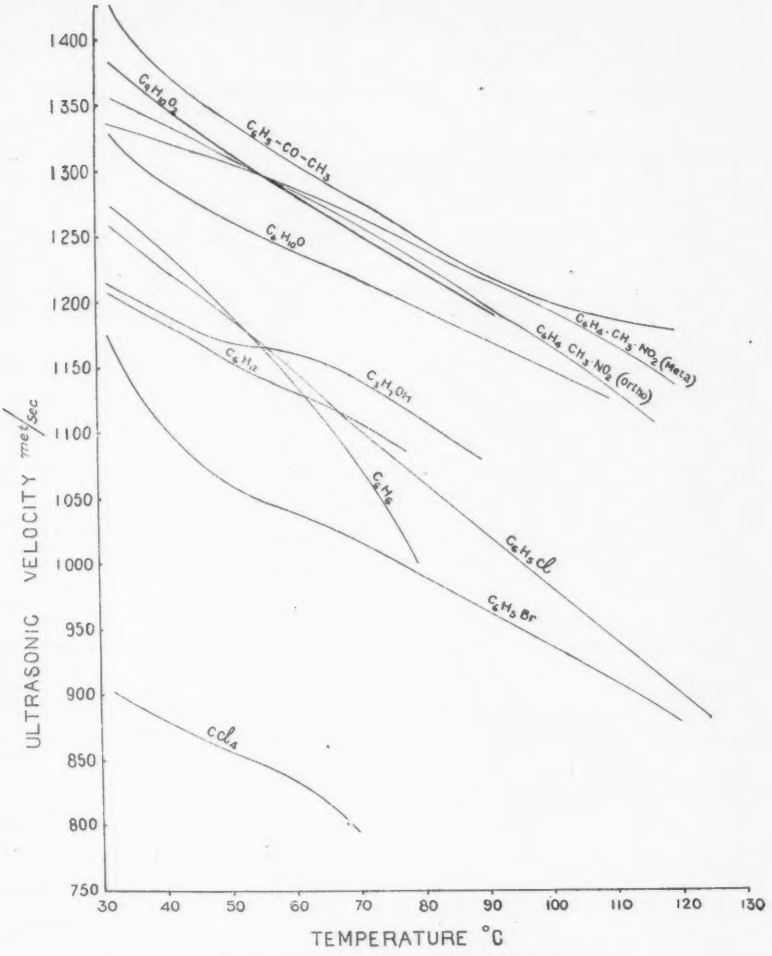


TABLE I. *Carbon Tetrachloride*

Author				Tyrer	
Temp. °C.	Density	Velocity met./sec.	Compressibility $\beta\phi \times 10^6$	Temp. °C.	Compressibility $\beta\phi \times 10^6$
32	1·572	903 (904)	79·1	29·09	78·38
40	1·557	882 (874)	83·6	38·29	83·88
50	1·538	858 (843)	89·4	47·10	90·78
60	1·521	833	96·1	57·72	99·28
70	1·505	791	107·6	67·63	106·74

TABLE II

Benzene

Author				Tyrer	
Temp. °C.	Density	Velocity met./sec.	Compressibility $\beta\phi \times 10^6$	Temp. °C.	Compressibility $\beta\phi \times 10^6$
31·5	0·867	1275 (1278)	71·9	30·52	72·35
40	0·857	1242 (1231)	76·7	36·38	75·64
50	0·848	1193 (1184)	83·9	42·76	79·80
60	0·840	1144	92·1	49·54	84·92
70	0·823 (?)	1076	106·2 (?)	49·67	84·62
79	0·816 (?)	998	124·6 (?)	65·40	97·58

TABLE III

Chlorobenzene

Author				Tyrer	
Temp. °C.	Density	Velocity met./sec.	Compressibility $\beta\phi \times 10^6$	Temp. °C.	Compressibility $\beta\phi \times 10^6$
32	1·095	1261 (1248)	58·2	35·53	61·83
40	1·085	1233 (1213)	61·4	43·97	65·37
50	1·073	1187 (1178)	67·1	52·79	69·59
60	1·063	1148	72·4	62·02	74·36
70	1·052	1110	78·2	71·67	78·87
80	1·040	1077	84·0	80·47	83·3
90	1·029	1022	94·1		
100	1·017	1000	99·7		
110	1·005	948	112·1		
120	0·994	910	123·3		

TABLE IV

Cyclohexane

Temp. °C.	Density	Velocity met./sec.	Compressibility $\beta\phi \times 10^6$
31·5	0·767	1205	89·7
42	0·760	1180	95·8
51	0·749	1155	101·4
61	0·739	1132	107·0
71	0·729	1110	112·9
78	0·722	1088	118·5

TABLE V

Bromobenzene

Temp. °C.	Density	Velocity met./sec.	Compressibility $\beta\phi \times 10^6$
32·5	1·480	1166	50·3
40	1·470	1108	56·2
50	1·455	1065	61·4
60	1·442	1035	65·6
70	1·428	1021	68·1
80	1·412	994	72·7
90	1·399	977	76·0
100	1·386	940	82·9
110	1·371	912	88·8
120	1·357	880	96·5

TABLE VI

Nitrotoluene (Ortho)

Temp. ° C.	Density	Velocity met./sec.	Compressibility $\beta\phi \times 10^6$
30	1·153	1356	47·8
40	1·145	1340	49·3
50	1·134	1316	51·6
60	1·124	1278	55·1
70	1·114	1250	58·2
80	1·105	1223	61·4
92	1·093	1197	64·7
100	1·085	1171	68·0
110	1·075	1130	73·8
120	1·065	1070	83·2

TABLE VII

Nitrotoluene (Meta)

Temp. ° C.	Density	Velocity met./sec.	Compressibility $\beta\phi \times 10^6$
28	1·144	1381	46·5
40	1·140	1323	50·8
50	1·129	1308	52·4
60	1·120	1278	55·3
70	1·110	1265	57·1
80	1·101	1237	60·2
90	1·092	1217	62·7
100	1·082	1198	65·3
110	1·073	1166	69·5
120	1·063	1137	73·8

TABLE VIII

Acetophenone

Temp. °C.	Density	Velocity met./sec.	Compressibility $\beta\phi \times 10^6$
32	1·018	1425	49·0
40	1·012	1371	53·3
50	1·002	1337	56·6
60	0·994	1305	59·9
70	0·985	1275	63·4
80	0·976	1245	67·0
90	0·968	1217	70·7
100	0·958	1203	73·0
110	0·949	1191	75·4
120	0·939	1177	77·8

TABLE IX

Cyclohexanone

Temp. °C.	Density	Velocity met./sec.	Compressibility $\beta\phi \times 10^6$
32	0·936	1322	61·9
40	0·928	1292	65·4
50	0·919	1263	69·2
60	0·910	1242	72·2
70	0·901	1217	75·9
80	0·891	1196	81·3
90	0·882	1171	83·8
100	0·872	1148	88·3
110	0·863	1136	91·0
120	0·853	1103	97·8

TABLE X

Benzyl Acetate

Temp. °C.	Density	Velocity met./sec.	Compressibility $\beta\phi \times 10^6$
32·5	1·044	1373	51·5
42·5	1·035	1340	54·6
50	1·028	1308	57·6
60	1·018	1278	61·0
70	1·008	1258	64·4
80	0·999	1223	67·9
90	0·990	1197	71·5
100	0·978	1165	76·35
110	0·969	1141	80·3
120	0·959	1121	84·0

TABLE XI

Propyl Alcohol (Iso)

Temp. °C	Density	Velocity met./sec.	Compressibility $\beta\phi \times 10^6$
31	0·805	1218	84·31
40	0·798	1192	90·3
50	0·789	1174	93·2
60	0·780	1162	96·9
70	0·770	1145	100·3
80	0·761	1116	107·0
90	0·751	1078	116·3

4. Discussion of Results

From Tables I, II and III, it can be seen that there is a fair agreement between the values reported by the earlier investigators and those of the author. In all the cases studied, the velocity of sound decreases with

increasing temperature. Amongst all the liquids studied, benzene exhibits the largest rate of fall. The average rate of fall is of the same order in all these liquids and is about 3 to 5 meters per second per degree. Ortho-nitrotoluene appears to have a slightly steeper temperature gradient of velocity than meta-nitrotoluene. Similarly the temperature gradient is more for chlorobenzene than for bromobenzene. In the case of *iso*-propyl alcohol, a point of inflexion is to be found at about 55° C.

5. *Summary and Conclusion*

Using the method based on the diffraction of light by ultrasonic waves, the sound velocities and the adiabatic compressibilities of eleven organic liquids have been determined at various temperatures in the range 30° C. to 120° C. Three of the liquids studied had been investigated earlier by Tyrer who used a piezometer and by Freyer, Hubbard and Andrews who used a sonic interferometer. The results of these authors are found to agree well with those obtained by the author. All the liquids exhibit a diminution of sound velocity with rising temperature, the rate being of the order of 3 to 5 metres per second per degree.

In conclusion, the author desires to express his best thanks to Prof. S. Bhagavantam for the interest he has taken in the work.

SOME PROPERTIES OF RECTILINEAR CONGRUENCES

By C. N. Srinivasiengar

(*Professor of Mathematics, Engineering College, Bangalore*)

Received July 16, 1940

1. Among the ruled surfaces passing through a given ray of a rectilinear congruence, there are two ruled surfaces characterized by the property that the parameter of distribution is a maximum or a minimum. These surfaces have been called *mean ruled surfaces* ('surfaces of distribution' by some writers). The central point of the ray with respect to either of these surfaces coincides with the middle point of the ray, the corresponding central planes are at right angles, being in fact the bisectors of the angles between the principal planes, and the sum of the parameters of distribution for the two mean surfaces is twice the parameter of distribution for either of the principal surfaces.[1]

The object of this paper is to obtain a neat generalization of these and of some other results.

Taking any direction dv/du on the director surface, the distance from the director surface of the central point of the surface corresponding to the direction chosen is given by

$$r = -\frac{a\,du^2 + (b+b')\,du\,dv + c\,dv^2}{e\,du^2 + 2f\,du\,dv + g\,dv^2}, \tag{1}$$

the notation being the same as in Weatherburn. If we choose the middle surface of the congruence as the director surface, and if the parameters are chosen so that the principal surfaces correspond to the parametric curves, we have

$$f = 0, \quad b + b' = 0, \quad ag + ce = 0. \tag{2}$$

The equation (1) can now be written

$$(a + er)\,du^2 + (c + gr)\,dv^2 = 0. \tag{3}$$

[1] *Vide* Weatherburn, *Differential Geometry*, Vol. I, Art. 99, where these and other properties referred to in this paper are proved.

The parameter of distribution corresponding to a given dv/du, referred to the above choice of parameters, is given by

$$p = \frac{b}{(eg)^{\frac{1}{2}}} + 2a\left(\frac{g}{e}\right)^{\frac{1}{2}} \frac{m}{e + gm^2}, \tag{4}$$

where $m = dv/du$.

For a given value of r on a given ray, equation (3) gives two values of m, say m_1 and m_2. Let the corresponding parameters of distribution be called p_1 and p_2. Then we have,

$$p_1 + p_2 - \frac{2b}{(eg)^{\frac{1}{2}}} = 2a\left(\frac{g}{e}\right)^{\frac{1}{2}} \left(\frac{m_1}{e + gm_1^2} + \frac{m_2}{e + gm_2^2}\right)$$

$$= 0, \quad \text{since } m_1 + m_2 = 0.$$

Hence,
$$p_1 + p_2 = \frac{2b}{(eg)^{\frac{1}{2}}} = \text{constant}.$$

If ϕ is the angle between the central plane for the surface corresponding to a given dv/du and the central plane for one of the mean surfaces, the parameter of distribution p for the surface is

$$p = \beta_1 \cos^2 \phi + \beta_2 \sin^2 \phi \tag{5}$$

where β_1 and β_2 are the parameters of distribution for the mean surfaces. Hence if

$$p_1 = \beta_1 \cos^2 \phi + \beta_2 \sin^2 \phi,$$

we get

$$p_2 = \beta_1 \sin^2 \phi + \beta_2 \cos^2 \phi.$$

Hence if ϕ is the angle corresponding to the value p_1, the angle corresponding to p_2 must be $90° \pm \phi$. But we can discriminate between these values and reject $90° + \phi$, by using the result[2]

$$r = \frac{\beta_2 - \beta_1}{2} \sin 2\phi, \tag{6}$$

for if we write $90° + \phi$ in place of ϕ, the sign of r is reversed, *i.e.*, we get a point on the other side of the middle point at the same distance.

We collect together these results as follows:

THEOREM.[3] *There are two surfaces through a given ray which have their central point on the ray at a given point. The sum of the parameters of*

---

[2] *Vide* Blaschke, *Differentialgeometrie*, Band 1, p. 208.

[3] The first part of the theorem was first proved by Delgleize (*Memoires de la Societe Royale des Sciences de Liege*, 1931, **16**, 1-9), and Ram Behari has proved the same by a somewhat different procedure, *Journ. Indian Math. Soc.*, (2), 1936, **2**, 92.

distribution for these two surfaces is a constant, as the point is varied. If the central plane for one of the mean surfaces makes an angle ϕ with the central plane for one of these two surfaces, it makes the angle $90° - \phi$ with the central plane for the other.

If the point is taken at either limit point, the two surfaces coincide, and hence the above-mentioned angle becomes 45° for a principal surface. If the point is taken at either focal point, one of the surfaces is a developable, so that at such a point p_1 is zero while $p_2 = \beta_1 + \beta_2$.

2. The elimination of m between (3) and (4) leads after simplification, and the use of the equation $ag + ce = 0$, in (2), to

$$p - \frac{b}{(eg)^{\frac{1}{2}}} = \pm \left(\frac{a^2}{e^2} - r^2\right)^{\frac{1}{2}}.$$

We enunciate this as follows:

THEOREM. *If we take two points A and B equidistant from the middle point of a ray on either side, the parameters of distribution for the pair of surfaces which have their central point at A are equal to those for the surfaces which have their central point at B.*

3. *Some formulae.*

We easily obtain

$$\tan \phi = \frac{\sqrt{e} - \sqrt{g}\, m}{\sqrt{e} + \sqrt{g}\, m},$$

whence from (4), we get

$$p - \frac{b}{\sqrt{eg}} = \frac{a}{e} \cos 2\phi$$

i.e.,

$$p - \frac{\beta_1 + \beta_2}{2} = \frac{\beta_1 - \beta_2}{2} \cos 2\phi.$$

From this and from (6), we get

$$r = \pm \left(p - \frac{\beta_1 + \beta_2}{2}\right) \tan 2\phi. \tag{7}$$

At a focal point, one of the values of p is zero, and let the corresponding ϕ be denoted by α. Then we know that

$$\tan \alpha = \pm \sqrt{\frac{-\beta_1}{\beta_2}}. \tag{8}$$

Using (8) in either (7) or (6), *we get the distance of a focal point from the middle point as numerically equal to* $\sqrt{-\beta_1 \beta_2}$. (9)

The result given by (8) can be generalized in two ways.[4]

(*a*) We have

$$\frac{p_1}{p_2} = \frac{\beta_1 \cos^2\phi + \beta_2 \sin^2\phi}{\beta_1 \sin^2\phi + \beta_2 \cos^2\phi}.$$

Hence

$$\tan^2\phi = \frac{\beta_1 p_2 - p_1\beta_2}{p_1\beta_1 - p_2\beta_2}.$$

Using $\beta_2 = p_1 + p_2 - \beta_1$, we obtain

$$\tan^2\phi = \frac{\beta_1 - p_1}{\beta_1 - p_2} = \frac{\beta_2 - p_2}{\beta_2 - p_1}. \tag{10}$$

The equation (8) is a particular case of (10) wherein $p_1 = 0$, $p_2 = \beta_1 + \beta_2$.

(*b*) Another generalization is the following equation, which is easily verified:

$$-\frac{p_1}{p_2} = \tan(\alpha - \phi)\tan(\alpha + \phi) \tag{11}$$

where α is given by (8).

Next, using (10) in (6), we obtain

$$\begin{aligned} r &= \pm\sqrt{(\beta_1 - p_1)(\beta_1 - p_2)} \\ &= \pm\sqrt{(\beta_2 - p_1)(\beta_2 - p_2)} \end{aligned} \tag{12}$$

which is a generalization of (9).

Also, (10) and (12) give

$$r\tan\phi = \beta_1 - p_1 = p_2 - \beta_2. \tag{13}$$

Finally, if O, F, L denote the middle point, a focal point, and a limit point respectively, we have

$$\begin{aligned} \mathrm{OL} &= \pm\frac{a}{e}, \quad \mathrm{OF}^2 = -\beta_1\beta_2 \\ &= \frac{a^2}{e^2} - \left(\frac{\beta_1 + \beta_2}{2}\right)^2. \end{aligned}$$

Using these in the equation of § 2, we get

$$p = (\mathrm{OL}^2 - \mathrm{OF}^2)^{\frac{1}{2}} \pm (\mathrm{OL}^2 - \mathrm{OP}^2)^{\frac{1}{2}} \tag{14}$$

where P is any point on the ray, and where $(\mathrm{OL}^2 - \mathrm{OF}^2)^{\frac{1}{2}}$ has a fixed sign, *viz.*, the sign of b.

---

[4] One other generalization is given by K. Ogura, *vide* Ram Behari's paper in *Journ. Indian Math. Soc.*, 1938, **3**, 110. Ogura's paper is not accessible to me.

SULPHURYL IODIDE

By M. R. Aswatha Narayana Rao
(Department of Chemistry, University of Mysore, Central College, Bangalore)

Received July 24, 1940
(Communicated by Prof. B. Sanjiva Rao)

Introduction

Attempts to prepare sulphuryl iodide have not hitherto met with any success. Odling[1] claims that the iodide is formed by the slow combination of sulphur dioxide and iodine in sunlight. But Schulze[2] has definitely established that the compound is not produced either by Odling's method or by the action of hydrogen iodide on sulphuryl chloride. The recent investigations of the present author on sulphur iodide[3] and thionyl iodide[4] have shown that these two substances are produced, when carbon tetrachloride solutions of the respective chlorides are treated with dry potassium iodide. A similar technique has now been adopted in the preparation of sulphuryl iodide.

Experimental

Reagents used.—(1) Sulphuryl chloride: Kahlbaum's 'purest quality' was used without further treatment. (2) Carbon disulphide (c.p. quality) was dried over phosphorus pentoxide and distilled. (3) Potassium iodide (Merck's extra pure) was finely powdered and dried over phosphorus pentoxide for 24 hours in a vacuum desiccator.

When a dilute solution of sulphuryl chloride in carbon tetrachloride (0·0005 molar) was shaken up (in the dark) with dry potassium iodide powder, the two reacted; but spectroscopic investigations indicated that sulphuryl iodide was not produced. The resulting solution was merely a mixture of iodine and sulphur dioxide. No evidence for the existence of sulphuryl iodide was obtained even when the experiment was tried at $-10°$ C. The reaction between sulphuryl chloride and potassium iodide was therefore tried at much lower temperatures. Carbon disulphide had to be used as solvent since carbon tetrachloride would freeze at temperatures below $-23°$ C.

The solution of sulphuryl chloride in carbon disulphide (0·0005 molar) was cooled to $-70°$ C. in a mixture of alcohol and solid carbon dioxide. The solution was then shaken up with potassium iodide in the dark for

2-3 minutes. Even at this low temperature, sulphuryl chloride and potassium iodide reacted giving rise to a violet solution. The solution was decanted free of potassium iodide and transferred quickly to two similar test-tubes. One of them was kept surrounded by the cooling bath while the other was allowed to attain the laboratory temperature. The violet colour deepened considerably in the latter. On keeping the test-tube back in the cooling mixture, the higher intensity of the violet colour persisted. This indicated that the carbon disulphide solution had some undecomposed sulphuryl iodide to start with which, however, decomposed into sulphur dioxide and iodine on raising the temperature. But when cooled again, the iodine and the sulphur dioxide did not recombine; hence the decomposed solution was deeper in violet colour. Since the fresh solution was only pale violet, it could be concluded that sulphuryl iodide was practically a colourless substance, like its chlorine analogue.

Spectroscopic Studies

The observations mentioned above were further confirmed by spectroscopic investigations. A Hilger Constant deviation spectrograph was used to obtain the absorption spectrum. The intensity of illumination and the period of exposure were maintained constant during each exposure. Spectrogram 1 was taken with a fresh solution of sulphuryl iodide (freed from potassium idoide) prepared at $-$ 70° C. as described above. Maintaining the absorption cell in the same position, the cooling bath was removed and the solution was kept at the laboratory temperature for 15 minutes. During this period, the violet colour became more intense. The absorption cell was cooled again to $-$ 70° C. and spectrogram 2 was then taken. Spectrogram 3 represents the absorption spectrum (at $-$70° C.) for a solution of iodine and sulphur dioxide in carbon disulphide which had the same concentration as the decomposed sulphuryl iodide solution.

A comparison of spectrograms 1 and 2 indicates that the intensity of transmission (in the violet region) is greater in the first spectrogram. This cannot be due to any temperature effect since both the solutions are kept at the same temperature. Hence it can be concluded that the iodine content of the solution when freshly prepared (spectrogram 1) is less than that of the same solution when the temperature is raised and the solution recooled (spectrogram 2). Spectrograms 2 and 3 are practically identical. This shows that after decomposition, the sulphuryl iodide solution is identical with that of a solution of iodine and sulphur dioxide. It is therefore to be concluded that the fresh solution contains both sulphuryl iodide and its products of decomposition (iodine and sulphur dioxide). On raising the termperature

however, sulphuryl iodide decomposes but the products of decomposition do not reunite on cooling. Hence the solution after decomposition contains more of iodine than the fresh solution.

Discussion

The spectroscopic evidence presented in this paper shows that sulphuryl iodide is formed on treatment of sulphuryl chloride solution (in carbon disulphide) with potassium iodide at $-70°$ C. The iodide decomposes rapidly when the temperature is raised, the products of decomposition being sulphur dioxide and iodine. Since the decomposition of sulphuryl iodide is irreversible, earlier reports about the combination of iodine with sulphur dioxide,[1] can hardly be correct. In proving the existence of sulphur iodide[3] and thionyl iodide,[4] the author has tried the action of sodium hydroxide solution on these two iodides. But this procedure cannot be employed to prove the formation of sulphuryl iodide since the products of reaction of sulphuryl iodide with alkali are identical with those of a mixture of sulphur dioxide and iodine when similarly treated.

Summary

(1) Spectroscopic investigations show that sulphuryl iodide is produced by the action of potassium iodide on a dilute solution of sulphuryl chloride in carbon disulphide at $-70°$ C.

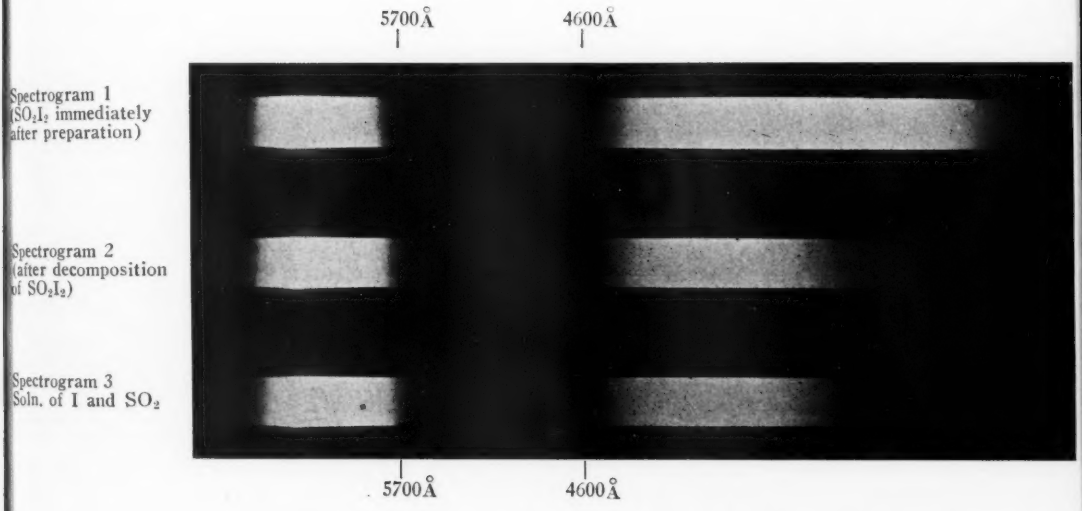
(2) At the laboratory temperature, the iodide decomposes almost immediately into sulphur dioxide and iodine which on cooling do not recombine.

Acknowledgment

The author takes this opportunity to express his sincere thanks to Professor B. Sanjiva Rao, for his keen interest in the work.

REFERENCES

1. Odling .. *J. Chem. Soc.*, 1854, **7**, 2.
2. Schulze .. *J. prakt. Chem.*, 1881, (2), **24**, 168.
3. M. R. A. Rao .. *Proc. Ind. Acad. Sci.*, 1940, **11**, 162.
4. ———— .. *Ibid.*, 1940, **11**, 185.



Absorption Spectrum of Sulphuryl Iodide solution in carbon disulphide

HETEROCYCLIC COMPOUNDS

Part XI. The Application of the Pechmann and the Kostanecki Reactions to γ-Orcacetophenone

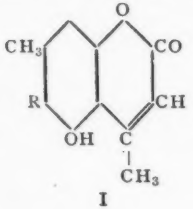
By R. D. Desai and (Miss) V. M. Vakil

(From the Department of Chemistry, St. Xavier's College, Bombay)

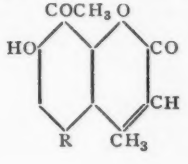
Received September 2, 1940

β-Orcacetophenone has been shown to condense with aceto-acetic ester in the presence of phosphoryl chloride or anhydrous aluminium chloride by Desai and Ekhlas,[1] as well as Shah and Shah,[2] with the formation of 5-hydroxy-6-acetyl-4 : 7-dimethyl coumarin (I, R = CH_3CO) and 5-hydroxy-4 : 7-dimethylcoumarin (I, R = H), the latter being formed from orcinol which was produced by the deacetylation of orcacetophenone. As we have worked out a satisfactory method of preparing γ-orcacetophenone (II), we thought of applying the Pechmann and the Kostanecki Reactions to this interesting dihydroxy-ketone.

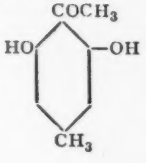
Acetoacetic ester condensed with γ-orcacetophenone or 2 : 6-dihydroxy-4-methylacetophenone either in the presence of concentrated sulphuric acid or phosphoryl chloride giving 5-hydroxy-4 : 7-dimethylcoumarin (I, R = H), and not a trace of the expected 7-hydroxy-8-acetyl-4 : 5-dimethylcoumarin (III, R = CH_3) was formed. This ketone, thus resembled 4-acetyl-1-naphthol which, according to Desai and Ekhlas (*loc. cit.*) underwent de-acetylation in the course of the Pechmann condensation. However, its behaviour was quite different from that of 2-acetylresorcinol which was found by Limaye[3] to condense readily forming 7-hydroxy-8-acetyl-4-methylcoumarin (III, R = H). Thus the presence of the methyl group in the *para*-position to the acetyl group brings about a marked change in the behaviour of γ-orcacetophenone, and it will be interesting to study the influence of other positive as well as negative groups in the place of methyl.



I

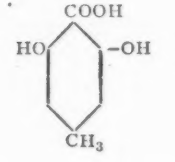


III

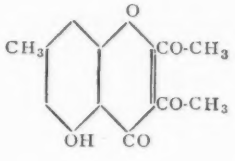


II

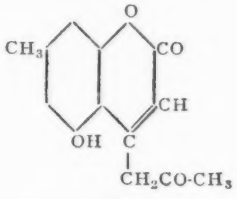
Vigorous acetylation of γ-orcacetophenone according to Kostanecki's method gave two products, one neutral and the other acidic. The neutral product (*A*) had the composition $C_{15}H_{14}O_5$ and melted at 103°, while the acidic product (*B*) having the composition $C_{13}H_{12}O_4$ melted at 137°. On leaving (*A*) in contact with concentrated sulphuric acid according to the method of Sethna and Shah,[4] an acidic product (*C*) melting at 141° was obtained. The general reactions as well as the mixed melting point showed that (*B*) was essentially identical with (*C*), but slightly contaminated with a small amount of an impurity. Alkaline hydrolysis of (*C*) gave *p*-orsellinic acid (IV) which was identified by comparison with an authentic specimen kindly supplied by Dr. R. C. Shah. Therefore, the constitution of (*C*) was 3-acetyl-2 : 7-dimethyl-5-hydroxychromone (V) while (*A*) was its 5-acetyl-derivative. When (*B*) was hydrolysed with alkali, *p*-orsellinic acid together with 5-hydroxy-4 : 7-dimethylcoumarin was produced. Therefore, the impurity present in (*B*) must be 4-acetonyl-5-hydroxy-7-methylcoumarin (VI) which is isomeric with (V). Thus though the main product of the Kostanecki Reaction is 3-acetyl-2 : 7-dimethyl-5-hydroxy-chromone, a small quantity of 4-acetonyl-5-hydroxy-7-methylcoumarin is also formed. Very recently Sethna and Shah (*loc. cit.*) have shown that substituted 4-acetonylcoumarins are exclusively produced during the Kostanecki acetylation of β-orcacetophenone. Thus it is quite clear that the course of this reaction is quite different in the case of the two isomeric orcacetophenones.



IV



V



VI

Experimental

Condensation of γ-orcacetophenone with aceto-acetic ester.—(1) A mixture of γ-orcacetophenone (1 g.), aceto-acetic ester (1 g.) and concentrated H_2SO_4 (5 c.c.) was left at the ordinary temperature for 24 hours, and poured over ice. The sticky solid on crystallisation from alcohol gave short needles, m.p. 256–58°, which was identified as 5-hydroxy-4 : 7-dimethylcoumarin by comparison with an authentic specimen. The mother-liquor did not furnish any other product. The same result was obtained on using 73 per cent. H_2SO_4.

(2) A mixture of the ketone (1 g.), aceto-acetic ester (1 g.), phosphoryl chloride (1 c.c.) and dry benzene (10 c.c.) was heated on water-bath under reflux for three hours. The benzene solution was poured out from some black, sticky precipitate that was formed at the bottom of the flask, and the residue extracted with three lots of benzene (10 c.c. each). After removing benzene from the combined extracts, the residue was crystallised from dilute alcohol when needles, m.p. 256°, were obtained, and were identified as 5-hydroxy 4: 7-dimethylcoumarin.

Kostanecki reaction with γ-orcacetophenone.—A mixture of γ-orcacetophenone (3 g.), anhydrous sodium acetate (3 g.) and acetic anhydride (15 c.c.) after being heated in an oil-bath at 175-80° for 20 hours, was poured into water, and the solid that slowly separated out was filtered off. The dry solid (1·4 g.) was shaken up with cold 5 per cent. NaOH, when part of it dissolved.

The insoluble portion A (0·5 g.) crystallised from dilute alcohol in cluster of needles, m.p. 103°. *5-Acetoxy-3-acetyl-2: 7-methylchromone* was soluble in most of the organic solvents, and its alcoholic solution did not give any coloration with ferric chloride. (Found: C, 65·6; H, 5·2; $C_{15}H_{12}O_4$ requires C, 65·7; H, 5·1 per cent.)

5-Hydroxy-3-acetyl -2: 7-dimethylchromone (*V*).—A pale-brown solution of the above product (0·3 g.) in concentrated H_2SO_4 (10 c.c.) was kept overnight, and poured over ice. The product which separated out crystallised from hexane in colourless needles, m.p. 141°. (Found: C, 67·5; H, 5·2; $C_{13}H_{12}O_4$ requires C, 67·2; H, 5·2 per cent.).

The chromone was soluble in most of the organic solvents, while its alcoholic solution gave a deep-violet coloration with ferric chloride. Its solution in dilute caustic soda solution as well as concentrated H_2SO_4 was yellow and non-fluorescent.

Hydrolysis of 5-hydroxy-3-acetyl-2: 7-dimethylchromone.—A solution of the chromone (0·2 g.) in 5 per cent. caustic soda (10 c.c.) was heated on sand-bath under reflux for one-and-half hours, cooled, filtered and acidified with concentrated HCl. The solid which was purified through a dilute sodium bicarbonate solution crystallised from hot water in needles, m.p. 165–66°, and identified as *p*-orsellinic acid by comparison with an authentic specimen.

The alkali-soluble substance (*B*) from the Kostanecki Reaction was recovered after acidification, and crystallised from alcohol in needles, m.p. 137°. This m.p. could not be raised by subsequent recrystallisations. Its

alcoholic solution gave a deep-violet coloration with ferric chloride, while its mixed m.p. with 5-hydroxy-3-acetyl-2: 7-dimethylchromone was 139°. (Found: C, 67·6; H, 5·1; $C_{13}H_{12}O_4$ requires C, 67·2; H, 5·2 per cent.)

Hydrolysis of B with 5 per cent. caustic soda and formation of p-*orsellinic acid and 5-hydroxy*-4: 7-*dimethylcoumarin.*—A solution of the product *B* (0·7 g.) in 5 per cent. caustic soda (15 c.c.) was heated on sand-bath under reflux for one-and-half hours. The solid (m.p. 143–46°) obtained on acidification of the mixture with concentrated HCl was treated with a solution of sodium bicarbonate which dissolved most of the solid leaving a residue (0·1 g.) which was identified as 5-hydroxy-4: 7-dimethylcoumarin while the alkaline solution gave, on acidification, *p*-orsellinic acid.

We thank Prof. R. N. Bhagwat, M.A., B.Sc., the Director of the Laboratories, and Rev. G. Palacios, S.J., Ph.D., D.D., the Principal, for their kind interest and provision of the facilities.

Summary

γ-Orcacetophenone undergoes deacetylation when condensed with acetoacetic ester in the presence of concentrated H_2SO_4 or phosphoryl chloride. Acetylation in presence of anhydrous sodium acetate gave a mixture of 5-acetoxy-2: 7-dimethyl-3-acetylchromone, 5-hydroxy-2: 7-dimethyl-3-acetyl chromone, and 4-acetonyl-5-hydroxy-7-methylcoumarin. Thus it differs essentially from its isomer β-orcacetophenone with respect to these reactions.

REFERENCES

1. Desai and Ekhlas .. *Proc. Ind. Acad. Sci.*, (A), 1938, **8**, 567.
2. Shah and Shah .. *J.*, 1938, 1424.
3. Limaye .. *Rasayanam*, 1936, **1**, 65.
4. Sethna and Shah .. *Jour. Ind. Chem. Soc.*, 1940, **17**, 239.

DIAMAGNETISM OF PHOSPHORUS

By S. Ramachandra Rao and S. Aravamudachari
(*From the Department of Physics, Annamalai University, Annamalainagar, South India*)

Received August 23, 1940

1. Introduction

From the magnetic point of view, phosphorus is an extremely interesting substance because of its allotropic modifications. The ordinary forms are the yellow (or white) and the red varieties. X-ray investigations indicate that probably yellow phosphorus is analogous with the cubic forms of antimony and arsenic; and red phosphorus with monoclinic antimony and arsenic (Mellor, 1928). The conclusions of different workers on the structure of red phosphorus are not in agreement. There is also Bridgman's black phosphorus which is probably hexagonal (Linck and Jung, 1925). Natta and Passerini (1930) have studied the crystal structure of white phosphorus. This substance when condensed at the temperature of liquid ammonia is cubic. Atomic positions however are yet undetermined. Another and non-cubic form is obtained by condensation at liquid-air temperatures. It is thus clear that most likely white phosphorus is cubic in structure with a probable superposition of another lattice.

The evidence from Raman effect also points to the same conclusion. Bhagavantam (1930) investigated the Raman effect of white phosphorus in the solid state. The characteristic frequencies obtained by him are 607, 468 and 374. Since the phosphorus molecule is known to contain 4 atoms, Bhagavantam (1930) has shown that the tetrahedral structure fits the results satisfactorily since such a structure would give only three frequencies. But for the particular law of forces adopted, the frequencies should have the ratio 2 : 2 : 1 but the observed frequencies deviate considerably, the ratio being 1·62 : 1·25 : 1. This divergence definitely indicates that the molecule does not possess a simple tetrahedral structure and that the force system in the molecule is more complicated. Venkateswaran (1935) studied the Raman spectrum of white phosphorus in four different states: (1) vapour, (2) liquid, (3) solid, and (4) solution in carbon disulphide. Small shifts in the Raman frequencies were obtained in the different states but Venkateswaran has not drawn any general conclusions.

The diamagnetic susceptibility of the two important forms of phosphorus were studied by Curie who obtained $-0{\cdot}84$ for the white and $-0{\cdot}66$ for

the red (Bhatnagar and Mathur, 1935). Honda (1910) and Owen (1912) found that white phosphorus had a specific susceptibility of $-0{\cdot}90$ which remained constant from $-170°$ C. to $120°$ C.

There is a large volume of convincing evidence to show that phosphorus dissolved in carbon disulphide exists as P_4 molecules (Mellor, 1928). If phosphorus exists as P_4 molecules in the solid state also and this molecule is non-polar, then on dissolving the solid in carbon disulphide, there should be no change of specific susceptibility.

It is the purpose of this investigation to examine this question carefully and find out whether there is any systematic variation of magnetic susceptibility when white phosphorus is dissolved in carbon disulphide.

2. *Experiment*

The magnetic investigation was carried out by the Gouy method. The experimental tube was about 30 cm. long and had an internal diameter of $0{\cdot}8$ cm. It was sealed at one end and a narrow tube about 4 mm. internal diameter is connected at the other end. The tube is cleaned thoroughly and dried. A mark is made exactly midway on the tube. Water distilled several times in an all-glass apparatus is poured into the tube up to the mark. The tube is next placed in a tall beaker containing water which is kept boiling. This procedure is to remove all traces of air from the water inside the tube. The experimental tube is next connected to a Hyvac pump and the pressure is brought to the lowest value possible. The tube is sealed off very near the top. The sealed glass is drawn off into the form of a hook for suspending the tube suitably from one arm of a balance.

After the magnetic work which will be described in the next section, the tube was broken open at the top. The water inside was poured out and the tube was thoroughly dried. It was then filled with a solution of phosphorus in carbon disulphide in the following manner.

The approximate volume of the tube up to the mark was 8 c.c. A graduated jar of 10 c.c. capacity fitted with a well-ground stopper was weighed. It was filled with about 9 c.c. of pure double-distilled carbon disulphide and weighed again. Small pieces of yellow phosphorus were dropped into the graduated jar to make up approximately any concentration.

Since the solution contained suspended impurity, it was filtered through two folds of filter-paper directly into the experimental tube. The work had to be done quickly and cautiously.

The tube was connected to the pumping equipment through a long capillary tube. The pressure was reduced by the pump rapidly. Violent

ebullition of the carbon disulphide solution was prevented by the long capillary tube. After a time the tube was sealed very near the upper end. Over forty solutions having different concentrations were prepared in this manner. Each tube was initially studied with water. The concentrations studied were within 25% of phosphorus by weight.

The specific susceptibility was determined by the Gouy method. The standard substance used was water whose volume susceptibility at 30° C. was assumed to be $-0{\cdot}720$.*

The specific gravities of the solutions of phosphorus in carbon disulphide were determined by weighing equal volumes of the solutions and carefully distilled water.

The concentration of phosphorus in solution was determined by evaporating to dryness (in vacuum) known mass of the solution and finding the mass of the solid left behind.

A careful measurement was made of the specific susceptibility of pure phosphorus. The substance was contained in small spherical glass bulbs and was obtained by evaporating to dryness (in vacuum) concentrated filtered solutions. The Curie method was adopted for this purpose. The mass of phosphorus taken during different measurements varied from about 20–100 mg.

3. *Results*

(*a*) *Phosphorus.*—The average of six measurements made with phosphorus gave a value of $-0{\cdot}840$ for the specific susceptibility. This compares favourably with $-0{\cdot}90$ obtained by Honda (1910) and Owen (1912). It also agrees with $-0{\cdot}84$ obtained by Curie.

(*b*) *Carbon disulphide.*—The specific susceptibility of carbon disulphide was obtained by the Gouy method. The mean of several measurements gave a value of $-0{\cdot}538$. This value agrees satisfactorily with those of other investigators.

(*c*) *Solutions of phosphorus in carbon disulphide.*—The results obtained with twenty-five solutions are given in the following table. The volume susceptibility, the relative density and the specific susceptibility are given in the second, third and fourth columns. The percentage concentration of phosphorus in the solution (expressed in grams of the substance present in 100 g. of the solution) is given in the fifth column. The sixth column gives the specific susceptibility calculated on the basis of the additive law.

---

* The specific susceptibility values in this paper are given in 10^{-6} unit.

The next column gives the difference between the calculated and observed values and the last column gives this difference for 100 g. of phosphorus in solution (at the same concentration).

No.	Volume Susceptibility κ	Rel. Density ρ	Specific Susceptibility χ_0	Concentration C	Calculated χ_c	$\chi_0 - \chi_c$	$\frac{\chi_0 - \chi_c}{C} \times 100$
	0·6742	1·254	0·538				
1	0·7040	1·283	0·549	3·1	0·547	0·002	0·06
2	0·7128	1·288	0·553	4·0	0·550	0·003	0·08
3	0·7339	1·296	0·566	6·5	0·557	0·009	0·14
4	0·7410	1·300	0·570	7·3	0·560	0·010	0·14
5	0·7473	1·302	0·574	8·2	0·563	0·011	0·13
6	0·7478	1·302	0·575	8·3	0·563	0·012	0·15
7	0·7589	1·304	0·582	9·8	0·568	0·014	0·14
8	0·7647	1·306	0·586	10·6	0·570	0·016	0·15
9	0·7755	1·310	0·592	12·0	0·574	0·018	0·15
10	0·7787	1·311	0·594	12·4	0·575	0·019	0·15
11	0·7806	1·312	0·595	12·8	0·577	0·018	0·14
12	0·7810	1·313	0·595	13·1	0·578	0·017	0·13
13	0·7847	1·317	0·596	14·5	0·582	0·014	0·10
14	0·7927	1·319	0·601	15·2	0·584	0·017	0·11
15	0·7965	1·321	0·603	16·0	0·586	0·017	0·11
16	0·8023	1·324	0·606	16·9	0·589	0·017	0·10
17	0·8044	1·329	0·608	18·3	0·593	0·015	0·08
18	0·8086	1·330	0·608	18·5	0·594	0·014	0·08
19	0·8113	1·330	0·610	19·1	0·596	0·014	0·07
20	0·8144	1·333	0·611	19·8	0·598	0·013	0·07
21	0·8156	1·335	0·611	20·2	0·599	0·012	0·06
22	0·8190	1·336	0·613	21·0	0·601	0·012	0·06
23	0·8208	1·339	0·613	21·2	0·602	0·011	0·05
24	0·8279	1·342	0·617	21·8	0·604	0·013	0·06
25	0·8297	1·345	0·617	22·0	0·604	0·013	0·06

It will be noted that the difference shown in column 7 is uniformly positive. The deviation in most of the cases is much larger than what may be safely allowed as error in the measurements. It appears therefore that the diamagnetic susceptibility observed is larger in every case than the calculated value. Hence it may be concluded that when white phosphorus is dissolved in carbon disulphide, the phosphorus in solution appears to have a larger diamagnetic specific susceptibility than in the solid state.

The change of susceptibility for 100 g. of phosphorus, given in the last column, is fairly constant in the range studied. At the highest concentrations studied this difference tends to diminish. On the whole, it may be safely concluded that at low concentrations the change of susceptibility for 100 g. of phosphorus is nearly constant.

4. Discussion

A similar variation was obtained by Varadachari and Subramaniam (1936) in the case of sulphur dissolved in carbon disulphide. They concluded that the increase in the diamagnetic susceptibility was due to the breaking down of the S_{16} complex into lower complexes in solution.

The increase in specific susceptibility obtained when 100 g. of phosphorus are dissolved in carbon disulphide is larger than the corresponding value for sulphur.

This increase may be explained in two ways. First we may assume that white phosphorus in the solid state contains higher complexes than P_4 and that when the solid is dissolved in carbon disulphide, these higher complexes break down to P_4. Such a process may bring about the increase of susceptibility.

A second possibility is that the tetrahedral molecule of phosphorus in the solid state is not completely non-polar. If it has a residual dipole moment due to any cause, the molecules of phosphorus would possess an intermolecular interaction. When the phosphorus is dissolved in carbon disulphide, this interaction is removed and this cause may bring about an increase of susceptibility.

According to Raman effect data of Venkateswaran (1935) the latter alternative is more likely since on dissolving white phosphorus, small shifts of the Raman frequencies are observed. No fundamental changes in the lines have been reported.

5. Summary

The magnetic susceptibility of solutions of white phosphorus in carbon disulphide has been examined at concentrations below 25% by weight. The

specific susceptibilities of pure phosphorus and carbon disulphide have also been determined. Phosphorus solutions were studied by the Gouy method.

It is found that the diamagnetic susceptibility observed when white phosphorus is dissolved in carbon disulphide, is larger than the value calculated from the additive law.

The change of susceptibility for 100 g. of phosphorus is fairly constant in the range of concentrations studied. This increase may be due to the white phosphorus in the solid state containing higher complexes than P_4. When the solid is dissolved in carbon disulphide, these higher complexes may break down to P_4 and bring about an increase of susceptibility. A second possibility is that the tetrahedral molecule of phosphorus in the solid state is not completely non-polar. The intermolecular interactions between the molecules of phosphorus would disappear on dissolving the solid, giving rise to an increase of diamagnetic susceptibility.

Raman effect data point out definitely that the latter alternative is more probable.

REFERENCES

Bhagavantam	..	*Ind. Jour. Phys.*, 1930, **5**, 35.
Bhatnagar and Mathur	..	*Magneto Chemistry*, 1935, p. 57.
Honda	..	*Ann. der Phys.*, 1910, **22**, 1027.
Link and Jung	..	*Z. Anorg. Chem.*, 1925, **147**, 288.
Mellor	..	*Treatise*, 1928, **8**, 755.
Owen	..	*Ann. der Phys.*, 1912, **27**, 657.
Passerini	..	*Nature*, 1930, **125**, 707.
Varadachari and Subramaniam		*Proc. Ind. Acad. Sci.*, (A), 1936, **3**, 428.
Venkateswaran	..	*Ibid.*, 1935, **2**, 260.

CHEMICAL INVESTIGATION OF INDIAN FRUITS

Part II. The Composition of the Oil from the Seeds of Indian Shaddock

By C. J. Dasa Rao, T. R. Seshadri
and
J. Veeraraghaviah
(From the Department of Chemical Technology, Andhra University, Waltair)

Received August 23, 1940

As a group the citrus fruits are very important. In the fruit industry, their value depends not only upon the quality of the juice, but also upon the possible utilisation of the by-products such as the peels and seeds. In a previous publication[1] the nature of the bitter principles present in the Indian Shaddock was dealt with. It was pointed out that the seeds are large and form a good percentage of the fruits. They yield about 40% of their weight of oil whose composition has now been studied.

As relevant to the present work it may be stated that Jamieson, Baughman and Gertler[2] investigated the fixed oil from grape fruit seeds obtained in America and found it to contain 26·6–27·6% of saturated acids. The percentage composition of the expressed oil was represented as olein 20·5, linolin 51·0, palmitin 20·1, stearin 7·6, lignocerin 0·1 and unsaponifiables 0·7. Van Loeseke[3] working on some problems in citrus products research found that grape fruit seed oil was rendered palatable by treatment with NaOH and charcoal. A solid at room temperature was obtained by hydrogenation of the oil in the presence of a catalyst. Bubbling air through the oil at elevated temperatures increased the viscosity and drying properties and when it was treated with sulphur chloride the oil yielded a rubber substitute similar to that obtained from cotton seed and maize oils.

The oil that was obtained by petroleum extraction of the shaddock seeds was employed for the present investigation. It was free from any bitterness, was golden yellow in colour and was edible. The mixed fatty acids that were isolated amounted to 90% of the oil and were composed of unsaturated acids 64% and saturated acids 36%. The acids were separated by the Twitchell's lead salt alcohol and ether method. The methyl esters of the liquid acids were fractioned under a reduced pressure of 0·2 mm. and the individual acids identified in each fraction by oxidation with alkaline permanganate according to the method of Lapworth and Mottram and subsequent comparison of the oxidation products with authentic samples.

The percentages of the various acids have been determined from these fractions. The individual liquid fatty acids were also identified and estimated by their bromo-derivatives as described by Eibner and Muggenthaler. The composition of the solid fatty acids was determined by making use of the barium acetate method of Heintz. The fatty acid composition was thus found to be palmitic acid 20·7%, stearic acid 15·3%, oleic acid 55·15%, linolic acid 8·03%, linolenic acid 0·48% and non-saponifiables 0·34%. It follows therefore that the major portion of the unsaturated acids of the shaddock seed oil consists of oleic acid whereas in the grape fruit seed oil linolic acid seems to be the main unsaturated component.

Experimental

1 kg. of the air-dried and powdered seeds were extracted with petroleum ether. 390 g. of a yellow oil was obtained which had the following characteristics:—

Taste not bitter (oil content of seeds)	39%
Specific gravity at 31° C.	0·9086
Refractive Index at 31° C.	1·4645
Saponification value	189·7
Iodine value	92·7
Free fatty acid (% as oleic acid) ..	15·37
Unsaponifiable matter	0·48

140 g. of the oil were treated with alcoholic sodium hydroxide and 126 g. of mixed fatty acids were obtained by treating the soda soap with mineral acid. The mixed acids had a mean molecular weight or saponification equivalent of 277·3 and an Iodine value 94·1.

Separation of solid and liquid acids.—120 g. of the mixed acids dissolved in 600 c.c. of 95% alcohol were refluxed for one hour with 90 g. of lead acetate dissovled in 600 c.c. of 95% alcohol. The lead salts that crystallised on leaving overnight were separated. The acids were liberated by treating separately the alcohol insoluble and soluble lead salts with hydrochloric acid.

	Weight in grams	%	Sap. Eq.	I. V.
Solid acids (lead salts insoluble in alcohol)	43·2	36	268·5	2·42
Liquid acids (lead salts soluble in alcohol)	76·8	64	281·6	104·2

Esterification and Fractionation of the esters of liquid acids.—64 g. of the liquid acids were converted into the methyl esters by boiling with methyl

alcohol in the presence of concentrated H_2SO_4. The resulting esters were rendered free of mineral acids by washing repeatedly with 5% solution of sodium carbonate and afterwards with water. The esters thus obtained weighed 63 g. and had saponification equivalent 295·2 and Iodine value 100·7.

Fractional distillation under 0·2 *mm. pressure. Liquid esters* 57·3 *g.*

Fraction	Temp. of still head	Weight of fraction (in grams)	Sap. val.	Sap. Eq.	Iodine number	Non-sap.	Acids identified
1	135–145° C.	18·0	189·8	295·6	100·8	nil	Oleic and linolic
2	147–150° C.	8·0	189·6	295·9	102·3	nil	,,
3	159·0° C.	13·5	189·7	295·7	105·9	nil	Oleic, linolic and linolenic
Residue		17·8	186·5	300·8	103·0	0·3 g.	,,

Corrected saponification equivalent of residue 295·7.

Composition of the fractions by weight

Fraction	Oleic	Linolic	Linolenic	Non-sap.	Total weight in grams
1	15·87	2·13	..	..	18·0
2	6·92	1·08	..	..	8·0
3	11·35	1·95	0·20	..	13·5
4	15·24	2·03	0·23	·30	17·8
Total	49·38	7·19	0·43	0·30	57·3
Calculated on 64% of total acids	55·15	8·03	0·48	0·34	64·0

Identification of the liquid acids in the various fractions was carried out as follows:—Each fraction was saponified and the liberated acids oxidised with potassium permanganate in dilute alkaline solution and the products examined. Fractions 1 and 2 gave dihydroxystearic acid (m.p. 130·5°) and tetrahydroxy stearic acid (m.p. 173°). Fractions 3 and 4 gave dihydroxy-stearic acid and tetrahydroxy-stearic acid in the precipitated acids and in the acid filtrate and acid melting at 204° C. corresponding to Linusic or Hexahydroxy-stearic acid was obtained. The above results of the oxidation clearly indicate the presence of oleic and linolic acids in the first two fractions and oleic, linolic and linolenic acids in the 3rd and 4th fractions.

Examination of the liquid acids by means of their bromo-derivatives.—2·43 g. of the liquid acids were dissolved in ether and the bromides were prepared by using liquid bromine. Separation of the ether insoluble and ether soluble bromides was carried out at −10° C. The ether insoluble bromide was separated and weighed; it was crystalline and melted at 180° C. without darkening during melting, thus showing that it consisted entirely of linolenic acid hexabromide. The ether soluble bromide was washed free of bromine and the ether removed. The residue was dissolved in boiling petroleum ether. On cooling the solution a crystalline precipitate separated and this was weighed. This had a m.p. of 111–13° showing that it consisted of linolic acid tetrabromide. The mother liquor was rendered free of the petroleum ether and the residue dried and weighed as oleic acid dibromide. From the weights of the three fractions the percentages of the various acids were calculated.

	% by Weight on the total bromides	Acid % on liquid acids	Acid % on the total acids	Acids in the fractions
1st fraction, hexabromide .. m.p. 180° C.	2·05	0·75	0·48	Linolenic
2nd fraction, tetrabromide .. m.p. 111–113° C.	27·00	12·60	8·07	Linolic
3rd fraction, dibromide ..	70·95	86·65	54·46	Oleic

Examination of the solid acids.—The solid acids being small in quantity could not be methylated and fractionated. Separation using Barium acetate was effected and the individual fractions were decomposed with hydrochloric acid to liberate the mixed solid fatty acids. The constant of the mixed acids were determined.

Fractional precipitation of the solid acids

Fraction	Weight of fraction in grams	M. P.	Sap. value	Sap. Eq.	Iodine value	Acids identified
1	4·0	64·5	201·6	278·4	2·3	Palmitic and stearic
2	4·0	56·4	214·7	261·3	3·4	,,
3	2·5	56·6	214·5	261·6	2·9	,,

Identification of the individual acids from the fractions was carried out as follows:—The acids liberated from each fraction after crystallisation from

ethyl acetate melted at 69·5° C. and there was no depression in melting point when mixed with pure stearic acid. The acid obtained from the mother liquor when subjected to repeated crystallisation melted at 62·0° C. and the melting point remained the same when mixed with pure palmitic acid. Thus there were only palmitic and stearic acids in the solid acid fraction.

Solid acid distribution by weight

Fraction	Palmitic (in grams)	Stearic (in grams)	Total (in grams)
1	0·80	3·20	4·0
2	3·24	0·76	4·0
3	2·0	0·5	2·5
Total	6·04	4·46	10·5
Calculated on 36% of total acids	20·7	15·3	36

Composition of the fatty acids in the glycerides

Acids	In liquid acids 64%	In solid acids 36%	Total	% by Weight	% on Mol. weight
Palmitic ..	..	20·7	20·7	20·7	22·43
Stearic ..	..	15·3	15·3	15·3	14·94
Oleic ..	55·15	..	55·15	55·46	54·90
Linolic ..	8·03	..	8·03	8·07	7·99
Linolenic ..	0·48	..	0·48	0·48	0·48
Non-Sap. ..	0·34	..	0·34	..	..

Summary

The component fatty acids of the oil obtained from the seeds of Indian shaddock have been examined. It contains very little of unsaponifiable matter and consists of the glycerides of palmitic acid 20·7%, stearic acid 15·3%, oleic acid 55·46%, linolic acid 8·07% and linolenic acid 0·48%.

LITERATURE REFERENCES

1. Seshadri and Veeraraghaviah .. *Proc. Ind. Acad. Sci.*, (A), 1940, **6**, 508.
2. Jamieson, Baughman and Gertler .. *Oil and Fat Industry*, 1930, 181.
3. Van Loeseke .. *Proc. Fla. Station, Hort. Soc.*, 1933, 38–43.

OCCURRENCE OF HERBACETIN IN THE FLOWERS OF THE INDIAN TULIP *(THESPASIA POPULNEA)*

By P. Suryaprakasa Rao and P. Prabhakara Reddy
(From the Department of Chemistry, Andhra University, Waltair)

Received August 16, 1940
(Communicated by Prof. T. R. Seshadri)

A few years ago[1] the flowers of *Thespasia populnea* were examined in these Laboratories by Neelakantam and Seshadri according to the general method described in connection with the study of the cotton flowers.[2] They analysed two samples collected in two different seasons and found that the composition of the pigment present in the two was not the same. The flowers secured from Coimbatore in October 1933 yielded as the main portion a non-glycosidic pigment named populnetin ($C_{14}H_8O_6$) melting at 270–75° (I), a small amount of its glucoside, populnin ($C_{20}H_{18}O_{11}$) melting at 228–30° (II) and a very small quantity of a third pigment which could be isolated only in the form of its acetyl derivative (III) melting at 182–85°. Another sample procured from Trichinopoly in the summer of 1936 contained populnin only.

During the course of their investigation Neelakantam and Seshadri noticed that the extract of the flowers was giving a small amount of an orange-red precipitate with neutral lead acetate, and that the crude samples of the pigments, before complete purification, showed slight but significant differences from the normal properties of a pure sample of either populnin or populnetin.

Treatment	Crude samples	Populnin	Populnetin
With dilute sodium hydroxide	Bluish-green colour	Deep yellow solution	Deep red solution
With neutral lead acetate ..	A small quantity of orange-red precipitate	No precipitate	No precipitate

These discrepancies indicated that the flowers contained, besides populnin and populnetin, a third substance which might be the pigment which could not be isolated pure but was obtained only in the form of its acetyl derivative (III).

With a view to obtain more of populnetin for further investigation, flowers secured from the Trichinopoly District in summer 1939 have been examined by us adopting the following procedure. The dried petals were extracted with alcohol and the extract was concentrated by distillation to a small bulk. It was then diluted with a large volume of water and the resulting solution was again concentrated on a water-bath. During this operation considerable amounts of resin separated out. It was filtered off and the clear filtrate was boiled under reflux with sulphuric acid in order to hydrolyse any glucosides present. After the hydrolysis only a small amount of a yellow substance separated out on cooling the aqueous solution. So it was extracted with ether four times and the extract on the removal of the solvent gave a good amount of the pigment. The yield of the pure substance was 8 gm. from 4,000 gm. of the dried petals. This pigment was found to be a tetrahydroxy flavonol giving a penta-acetyl derivative on acetylation, and was noticed to be completely different from populnetin in all its properties as shown in the following table:

Property	Populnetin	The pigment isolated now
1. Molecular formula	$C_{14}H_8O_6$, H_2O	$C_{15}H_{10}O_7$, H_2O
2. Melting point	270–75°	280–82°
3. Reaction with neutral lead acetate ..	No precipitate	Red precipitate
4. Reaction with basic lead acetate ..	Yellow-orange precipitate	Red precipitate
5. Reaction with ferric chloride ..	Pale green	Olive green
6. Alkaline buffer solutions	Does not give prominent colours	Very prominent and rapid colour changes: Yellow-olive green–Violet-blue
7. Treatment with con. H_2SO_4 ..	Yellow solution with a green fluorescence	Dissolves forming a yellow solution
8. M.P. of the acetyl derivative ..	127–29°	190–93°

From a consideration of the melting points, it seemed probable that the acetyl derivative obtained now might be the same as the one (III) isolated before by Neelakantam and Seshadri. The sample of these authors, on repeated recrystallisations, became purer, melting at 188–90°. The identity of these two acetyl derivatives was established by taking the mixed melting point, which remained undepressed. The properties of the aglucone indicated that the substance might be the tetrahydroxy-flavonol, herbacetin originally obtained by Neelakantam, Rao and Seshadri[3] from the herbaceum

cotton flowers and later shown to be present in the indicum cotton flowers also[4,5]. The identity of the aglucone as herbacetin was confirmed by comparing its acetyl derivative with an authentic sample of acetylherbacetin. To state the results in terms of the aglucones, the first sample of the *Thespasia* flowers yielded both populnetin and herbacetin (very small) and the second one only populnetin. The third sample contained mainly herbacetin and little of populnetin. It is thus quite evident that both populnetin and herbacetin are present in the flowers of *Thespasia populnea* and their relative proportion seems to vary considerably depending on the season of collection of the flowers.

The authors wish to thank Prof. T. R. Seshadri for his interest in this work.

REFERENCES

1. Neelakantam and Seshadri .. *Curr. Sci.*, 1938, **7**, 16.
2. ———, Rao and Seshadri .. *Proc. Ind. Acad. Sci.*, (A), 1935, **1**, 887; *ibid.*, 1935, **2**, 490.
3. ———— .. *Ibid.*, 1935, **2**, 494.
4. Neelakantam and Seshadri .. *Ibid.*, 1936, **4**, 58.
5. Suryaprakasa Rao and Seshadri *Curr. Sci.*, 1938, **7**, 227.

A NOTE ON CERTAIN CONSTITUTIONAL FACTORS CONTROLLING VISIBLE FLUORESCENCE IN COMPOUNDS OF THE BENZO-PYRONE GROUP

By S. Rangaswami and T. R. Seshadri

(From the Department of Chemical Technology, Andhra University, Waltair)

Received August 13, 1940

Certain groups of organic compounds are noted for their capacity to exhibit fluorescence and this has been frequently found to be of help for purposes of identification. The benzo-pyrone group is one such and several compounds coming under the category of coumarins, chromones, flavones and *iso*-flavones have been known to exhibit marked fluorescence. However, no systematic study seems to have been attempted till now on the influence of constitutional factors in controlling this property.

As a result of synthetic work in progress in these laboratories a large number of coumarin derivatives have become available. They have now been studied with reference to their capacity to exhibit fluorescence. The observations were made in ordinary sunlight with carefully purified materials in very dilute solutions; in almost all cases the solutions were colourless or pale yellow when fluorescence was exhibited. Coumarin, 7-methyl-coumarin, 4:7-dimethyl- and 3:4:7-trimethyl-coumarins, 6-nitro- and 6-amino-coumarins and coumarino-7:8-α-pyrone did not exhibit fluorescence either in concentrated sulphuric acid or in alkaline solution. The results obtained with other compounds are summarised in the accompanying table.

Name of compound	Nature of the fluorescence in ordinary sunlight	
	In aqueous sodium hydroxide	In conc. sulphuric acid
7-Hydroxycoumarin	Blue (disappears in about 10 minutes)	Violet blue
7-Methoxycoumarin	Nil	Bluish violet
7-Acetoxycoumarin ..	Pale blue turning bright blue (slowly disappears)	Do.
7-Hydroxy-4-methylcoumarin	Strong blue (disappears after about 1 hour)	Do.
7-Hydroxy-4-methyl-6-bromocoumarin ..	Blue	Nil
7-Hydroxy-4-methyl-6:8-dibromocoumarin ..	Do.	Nil
7-Methoxy-4-methylcoumarin	Nil	Bluish violet

Name of compound	Nature of the fluorescence in ordinary sunlight	
	In aqueous sodium hydroxide	In conc. sulphuric acid
7-Acetoxy-4-methylcoumarin	Very pale violet fast turning bright blue (slowly disappears)	Violet
7-Hydroxy-4 : 8-dimethylcoumarin	Pale blue (persists even after 5–6 hours)	Very feeble blue
7-Acetoxy-4 : 8-dimethylcoumarin	At first nil; but slowly develops pale blue due to hydrolysis	Feeble blue
7-Allyloxy-4 : 8-dimethylcoumarin	Nil	Blue
7-Hydroxy-5-methylcoumarin	Intense blue (disappears in 20–30 minutes)	Intense blue
7-Hydroxy-3 : 4-dimethylcoumarin	Blue	Violet blue
7-Hydroxy-3 : 4-dimethyl-8-nitrocoumarin ..	Nil	Nil
7-Hydroxy-6-allyl-4 : 8-dimethylcoumarin ..	Blue (disappears after about 2 hours)	Blue
7-Hydroxy-8-formylcoumarin	Nil	Nil
7-Hydroxy-8-acetyl-4-methylcoumarin ..	Nil	Nil
7-Hydroxy-6-acetyl-4 : 8-dimethylcoumarin ..	Nil	Nil
7-Hydroxy-3 : 6-dibromo-4 : 8-dimethylcoumarin	Nil	Nil
7-Hydroxy-5-methyl-3-carboxycoumarin ..	Intense blue (disappears in ½–1 hour)	Pale blue
7-Hydroxy-5-methyl-3-carbethoxycoumarin ..	Intense blue (persists even after 5–6 hours)	Pale blue
5-Hydroxy-7-methylcoumarin	Nil	Nil
5-Hydroxy-4 : 7-dimethylcoumarin	Nil	Nil
5 : 7-Dihydroxycoumarin	Nil	Nil
5-Hydroxy-4 : 7-dimethyl-6-carbethoxycoumarin	Nil	Nil
5-Hydroxy-4 : 7-dimethyl-6-carboxycoumarin ..	Nil	Nil
5-Hydroxy-7-methyl-3 : 8-dicarbethoxycoumarin	Nil	Nil
5-Hydroxy-7-methyl-8-carboxycoumarin ..	Nil	Nil
Coumaric acid	Very pale green	Nil
Mercurated coumaric acid	Bright green	Nil
Umbellic acid	Nil	Nil
Mercurated umbellic acid	Nil	Nil
5-Nitrocoumaric acid	Nil	Nil

From the data given above and those found scattered in the literature the essential requirement for the production of fluorescence by the coumarins seems to be the existence of a hydroxyl group in the 7-position. In neutral solution 7-hydroxycoumarin itself is non-fluorescent; the fluorescene is developed in alkaline (*e.g.*, aqueous sodium hydroxide) and strong acid (sulphuric acid) media, the colour of the fluorescence being the same or slightly different in the two solutions. It is obvious that the fluorescence found in these cases is the property of the ions. The fluorescence exhibited in strong sulphuric acid solution is lost on pouring it into water; this is due to the fact that the oxonium ions to which the fluorescence in the acid solution is due are very unstable in the presence of a large volume of water. The intensity of the fluorescence is markedly greater in the alkaline solutions than in the solutions in sulphuric acid. The gradual disappearance of the fluorescence in alkaline solutions of umbelliferone and its derivatives can be attributed to the opening of the pyrone ring leading to the formation of the corresponding coumarinic acids. This opening of the ring is known to take place with lesser speed when substituents are present in the pyrone ring and the greater persistence of the fluorescence in such cases agrees with expectations. It may, however, be mentioned that the rapidity of the change is dependent on the amount of alkali added. In our observations we have employed sufficient sodium hydroxide to make the strength of the solution about one per cent.

When the hydroxyl is converted into a methoxyl or allyloxyl it is significant that there is no fluorescence in alkaline solution whereas there is fluorescence in sulphuric acid. No ions can be produced in alkaline solution in these cases. 7-Acetoxycoumarin, however, exhibits a pale blue fluorescence even in alkaline medium, probably because of the ease with which it is hydrolysed to umbelliferone. The fluorescence which is at first practically nil becomes more and more intense on standing for some time as a result of progressive hydrolysis; the resulting solution thereafter behaves just like an alkaline solution of umbelliferone ultimately becoming non-fluorescent. A similar behaviour is noticed with the 4-methyl homologue of 7-acetoxycoumarin.

Regarding the influence of other substituent groups on the fluorescence exhibited by 7-hydroxycoumarin it may be said that alkyl groups in the 4- and 5- positions enhance and in the 8-position reduce considerably the intensity. Formyl, acetyl and nitro-groups in the *ortho*-position (8-position) to the hydroxyl completely inhibit fluorescence and the introduction of bromine atoms reduces the intensity markedly and in some cases removes all fluorescence. It has been further noted that carbethoxy and carboxy groups in the 3-position enhance greatly the fluorescence and make it become

intense blue; it is noteworthy that these compounds exhibit strong fluorescence (blue) even in neutral alcoholic solutions.

When the hydroxyl group is present not in the 7- but in the 5-position a deep yellow coloured solution is produced without any fluorescence. This is a characteristic difference highly useful for the allocation of hydroxyl groups to the various nuclear positions in the aromatic ring. The existence of a 5-hydroxyl further counteracts the original property of the 7-hydroxy group of producing fluorescence and hence 5 : 7-dihydroxy-coumarins are devoid of the property of exhibiting fluorescence. A similar lack of fluorescence has been recorded in the case of 7 : 8-dihydroxycoumarin. But 6 : 7-dihydroxy-coumarin (aesculetin) is said to give a weak blue fluorescence.

Unlike coumarin, coumaric acid exhibits a feeble fluorescence in alkaline solutions but not in sulphuric acid medium. This is considerably intensified by the existence of even traces of mercury in the compound. It has been noted during the preparation of coumaric acid by the simple method described by Seshadri and Rao[1] that if the procedure has been carried out correctly and no mercuration has taken place the coumaric acid solution is simply yellow with only a feeble fluorescence. On the other hand any presence of mercury is indicated by a brilliant green fluorescence; this combined mercury can be removed by passing hydrogen sulphide into the solution. 4-Methyl-coumaric acid obtained from 7-methylcoumarin behaves in a similar fashion. The presence of a hydroxyl substituent, however, makes a great difference; umbelliferone loses its fluorescence in alkaline solution as has already been pointed out owing to the opening out of the pyrone ring with the formation of the hydroxy-coumarinic acid. The addition of mercuric oxide accelerates the loss of fluorescence since umbellic acid (4-hydroxy-coumaric acid) and its mercuration products that may be formed do not exhibit any fluorescence in alkaline or acid solutions.

From a study of past literature relating to the incidence of fluorescence in the flavone, *iso*-flavone and chromone series the first point that strikes one is that it is very widely met with in concentrated sulphuric acid medium but almost absent in alkaline solutions. 2-Methyl-3-methoxy-7-hydroxy-chromone and 2-methyl-7-hydroxy-*iso*-flavone seem to be the only two compounds that exhibit fluorescence in alkaline solutions. In this respect the γ-pyrone derivatives differ fundamentally from the coumarins wherein fluorescence is much more prominent in alkaline than in sulphuric acid solutions. Further in contrast to the coumarin series the flavones do not seem to depend on the presence of a hydroxy group for exhibiting fluorescence. It has been recorded that the colourless solution of simple flavone itself in strong sulphuric acid exhibits a strong violet blue fluorescence. Nor does

the position occupied by a hydroxyl group in the different rings seem to have any specific influence on the incidence of fluorescence, since 3-, 6-, 7- and 4′-hydroxy-flavones are all said to exhibit fluorescence. The only reasonable generalisation seems to be that all the simple hydroxy derivatives of chromones, flavones and *iso*-flavones are fluorescent. The presence of a large number of hydroxyl groups however has an adverse effect. Thus kæmpferol (3 : 5 : 7 : 3′-tetrahydroxyflavone) is fluorescent (blue) but not quercetin (3 : 5 : 7 : 3′ : 4′ :-pentahydroxyflavone). It may however be noted that the inhibitory influence of the large number of hydroxyl groups is considerably removed when some of them are methylated; rhamnetin (7-methyl ether of quercetin) and *iso*-rhamnetin (3′-methyl ether of quercetin) are fluorescent (greenish blue and green respectively) and so also is 3 : 3′ : 4′-trimethylquercetin.

Regarding the influence of alkyl and acyl groups situated in different positions in the chromone and flavone ring-systems no data seem to have been collected till now. Hence a few substances which are derivatives of 7-hydroxy-chromone and flavone and available in our laboratories have now been examined and as the observations are likely to be informative and useful they are given in the following table:

Name of compound	Nature of the fluorescence in conc. sulphuric acid
7-Hydroxyflavone	Deep blue
7-Acetoxyflavone	Blue deepening with time
7-Methoxyflavone	Blue
7-Allyloxyflavone	Strong blue
7-Hydroxy-8-methylflavone	Nil
7-Hydroxy-8-allylflavone	Green
7-Hydroxy-6 : 8-diallylflavone	Do.
7-Hydroxy-3-methoxyflavone	Very pale blue
7-Hydroxy-3-methoxy-8-methylflavone	Nil
7-Hydroxy-3-benzoylflavone	Nil
7-Hydroxy-8-formyl-3-methoxyflavone	Nil
7-Hydroxy-3-methoxy-2-methylchromone	Blue
7-Allyloxy-3-methoxy-2-methylchromone	Do.

Name of compound	Nature of the fluorescence in conc. sulphuric acid
7-Hydroxy-8-allyl-3-methoxy-2-methylchromone	Pale green
7-Hydroxy-3-methoxy-2-styrylchromone	Green
7-Hydroxy-3-acetyl-2-methylchromone	Nil
7-Hydroxy-8-formyl-3-methoxy-2-methylchromone	Nil

Regarding the flavones conversion of the 7-hydroxyl group into the acetoxyl, methoxyl and allyloxyl does not produce any marked change. A methyl group situated in the 8-position which is *ortho* to the hydroxyl removes the capacity to fluoresce; whereas one or two allyl groups similarly located only modify the colour of the fluorescence and convert it to green. An acyl group present in the 3- or in the 8- positions inhibits the fluorescence. The influence of substituent groups on the fluorescence exhibited by the chromones seems to be on the same lines as above though there are small differences particularly of intensity.

REFERENCE

1. Seshadri and Rao .. *Proc. Ind. Acad. Sci.*, (A), 1936, **3** 294.

SECONDARY ELECTRON EMISSION OF NICKEL AT THE CURIE POINT*

By P. S. Varadachari

(*Annamalai University, Annamalainagar, South India*)

Received August 23, 1940

(Communicated by Prof. S. Ramachandra Rao, M.A., Ph.D., D.Sc.)

1. Introduction

The phenomenon of the secondary electron emission from metal faces has been studied by a large number of workers in recent years. An excellent summary of these studies is given by Warnecke (1936).

The general disposition of the variations of the secondary electron coefficient at increasing applied potentials may now be taken to be definitely established. Rao (1930) has shown that as the applied potential is increased from zero, the ratio of the secondary to the primary current increases rapidly, attains a maximum value in the neighbourhood of 3 volts and then decreases gradually up to about 20 volts. The value then rises steadily, attaining a maximum at a potential of about 500 volts and thereafter decreases slowly. These results were obtained with polycrystalline nickel; but the same general conclusions have been found to hold good in the case of other metals. The absolute value of the secondary electron coefficient at any applied potential and the potential at which the coefficient attains a maximum value are found to vary from metal to metal.

The similarity of the phenomenon of soft X-ray excitation and secondary electron emission led Richardson (1930) to postulate a mechanism for the observed velocity distribution of the secondary electrons. Rudberg (1930) had previously discovered the presence of three groups of electrons in the secondary emission. The first group in accordance with these conclusions contains electrons which return with the same velocity as the primary. Those electrons which undergo inelastic collisions with the orbital and structure electrons and are hence returned with some loss of energy constitute the second group. Finally there is the third group of electrons which include the slow secondary electrons.

*A preliminary account of this work was communicated to the Proceedings of the Indian Science Congress Session held in January 1938. The publication of the detailed report has unfortunately been delayed till now.

Richardson (1930) suggested that the high-energy group of electrons resulted from inelastic encounters of the incident electrons with the structure electrons which attained states of higher energy. On their return to the ground state, soft X-rays and low-energy secondary electrons were ejected. Richardson's picture explained a complicated process and accounted for the remarkable similarity in property between soft X-ray excitation and secondary electron emission.

Studies on the efficiency of secondary electron emission by Rao (1933) established the conclusion that the first group of secondary electrons is large at applied potentials below 10 volts but becomes small at higher potentials. The efficiency of the second and third groups is small at low primary potentials and increases rapidly as the potential is raised.

It is necessary to set forth these considerations at some length to appreciate the experimental work of Tartakowsky and Kudrjawzewa (1932), who found that the secondary electron coefficient showed a sudden decrease in value at the Curie point in the case of nickel. Their apparatus consisted of a nickel plate which was heated by a tungsten filament fixed on one side. The primary electrons were incident on the other side. Part of the secondary emission fell into a Faraday chamber and was measured with an electrometer.

Treloar and Landon (1938) have pointed out the drawbacks in the arrangement employed by Tartakowsky and Kudrjawzewa (1932). No precise physical significance can be attached to the results of the latter workers unless the following conditions were satisfied over the temperature range adopted: (1) constancy of angular distribution of the emitted electrons; (2) constancy of energy distribution of the emitted secondaries; (3) constancy of potentials on the glass walls; (4) absence of stray magnetic fields due to the current in the filament used to heat the target. It is obvious that these conditions were not satisfied in their experiments. They found that at an applied potential of 30 volts, the secondary electron current increased when the temperature of nickel was raised from 150° to 350° C. An abrupt fall was obtained at the Curie temperature (358° C.) and thereafter there was a continuous increase. Working with a copper target, the secondary emission was found to increase linearly with temperature. Even this conclusion is at variance with the results of Krefft (1928) who found that the secondary emission coefficient of tungsten was constant in the range from 20° to 1450° C.

Hayakawa (1933) has reported similar observations with iron, cobalt and nickel. In fact he has studied the transformations of metals by secondary

electron emission. His method consisted in collecting all the secondary electrons emitted and the electrical connections adopted were similar to those of Rao (1930). Treloar and Landon (1938) have drawn attention to the existence of several discrepancies in the results of Hayakawa. The secondary coefficient showed large variations at temperatures corresponding to the Curie point in the case of nickel and to transformation points in the cases of cobalt and iron. Hayakawa interpreted his results in the light of Richardson's theory of structure electrons.

Rao (1937) studied the excitation of soft X-rays and the emission of photoelectrons from nickel at temperatures in the neighbourhood of the critical point of nickel. His results showed no abrupt or anomalous variations at the Curie temperature. He drew specific attention to the inherent difficulties present in the conclusions of Hayakawa (1933) and Tartakowsky and Kudrjawzewa (1932).

Treloar and Landon (1938) investigated the secondary emission from nickel, cobalt and iron. They obtained no sudden changes at the transformation or Curie points. In the case of nickel, they observed a slight and gradual decrease of the secondary emission coefficient when the temperature of the metal target was reduced from 525° to 110° C. They attribute this change to the probable adsorption of gas by the metal surface.

The following experiments were undertaken with a view to investigate the secondary emission from nickel with great care. The heating method adopted was efficient and special investigations were carried out to study the influence of imposed magnetic fields on the secondary emission coefficient. The results show that the secondary coefficient is constant to within 1% in the range 30°–470° C.

2. *Experiment*

It was felt that a real test should be made with the target thoroughly degassed since internal changes at the Curie point may result in the alteration of the gas content of nickel, which factor by itself may produce several changes in the observed secondary emission.

The experimental method adopted was similar to that of Rao. The tube was made of pyrex (by the Scientific Instrument Co., Allahabad) and is illustrated in Fig. 1. All the metal parts except the filaments were made of thin sheet silver. F_1 is the filament of tungsten which gives the primary beam of electrons. A is a shield outside the filament with an aperture of diameter 7 mm. The part B is the electron gun which gives a beam of electrons, the diameter of the beam being 3·5 mm. The primary beam

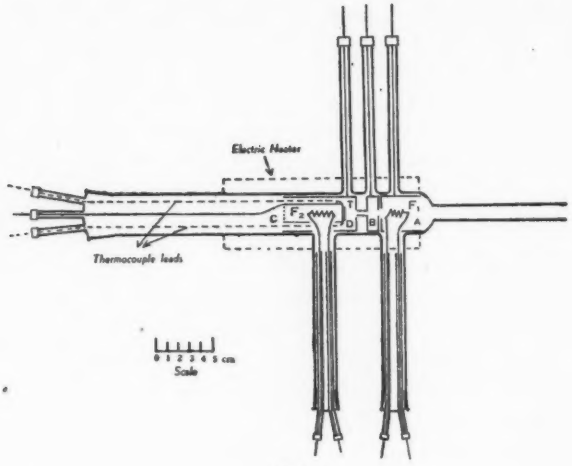


FIG. 1

falls on the target T of pure nickel fixed on the closed end of a hollow metal cylinder C. To facilitate degassing the cylinder and the target, a filament F_2 is arranged within the cylinder. The secondary electrons are collected by a shield D outside the cylinder. All the joints and seals were made with tight fitting brass caps and small quantities of hard sealing wax.

During working conditions the pressure inside the tube was reduced to some value less than 10^{-6} mm. The vacuum consisted of a Cenco hyvac pump and a three-stage mercury diffusion pump. Two traps, one of which contained coconut charcoal, were cooled with a mixture of carbon dioxide snow and ether. The pressure inside was measured with a Macleod gauge.

The electrical connections adopted are shown in Fig. 2. The heating currents for the filaments F_1 and F_2 were supplied by storage batteries. The

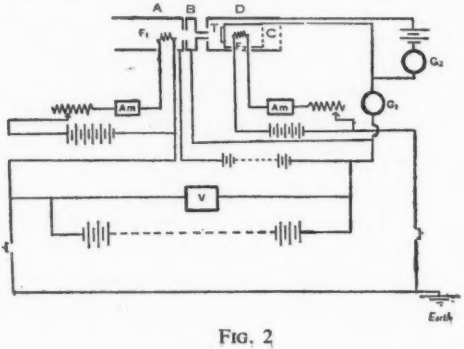


FIG. 2

primary and secondary currents were measured with galvanometers G_1 and G_2. The required potentials for bombardment were taken from a high tension battery of Dagenite 10-volt accumulators.

The shield A around the filament F_1 was usually maintained at 50 V higher than the canal B and the target. A fairly strong electron beam was thus obtained even at moderate potentials.

An additional positive potential of 4 V on the shield with respect to the target was enough to prevent any reflection or emission of electrons from the shield. The electrons reflected back directly through the opening of the shield C will be lost. But since the solid angle subtended by the opening at the centre of the target is small, the decrease will be small. Also in comparative measurements, this decrease will have no influence.

The heating of tube was effected by enclosing the tube in an electric heater containing a suitable number of turns of (S.W.G. No. 22) nichrome wire. The temperature of the target was measured with the aid of a thermoelectric thermocouple, consisting of a wire of pure platinum and another wire of an alloy of platinum and 10% rhodium. This standard thermocouple has been calibrated by the National Physical Laboratory and from the observed electromotive force of the couple, the temperature may be found.

The metal parts were degassed thoroughly by raising the tube to about 500° C. inside the electric heater. The cylinder and the target were simultaneously degassed by heating them to bright red heat by electronic bombardment. Much of the success of the experiment depends on the state of the metal surface and hence special precautions were taken to degass the target completely.

The measurements of the primary and secondary currents were made both when the temperature of the target was increased and when it was gradually decreased.

The target was raised to high temperatures by sending a suitable current in the filament F_2 (Fig. 2). A blank experiment was conducted showing the temperatures reached by the target for different currents in F_2. This enabled one to raise the target to any desired order of temperature, the correct temperature being found in each case by the thermocouple.

An accurate estimation of the applied potential to which the electrons arising out of the filament F_1 are subjected is a matter of some difficulty on account of the uncertain values of the corrections to be applied. These corrections are (1) correction for the initial emission velocity of the electrons

which is about $+\frac{1}{4}$ volt at the temperature of the filament, (2) correction for the drop in potential along the filament which works to about $+1{\cdot}5$ volts and (3) correction for the contact difference of potential between the hot cathode and the nickel target. The last correction is not capable of being correctly estimated. But in this investigation, we are not concerned with the absolute value of the applied potential. What concerns us is the conclusion that increasing the temperature of the target will not modify the total correction to any significant degree.

3. *Results*

Rao (1930) has obtained evidence to show that the ratio i_s/i_p varies with i_p as the primary current is increased from 0·2–5 microamperes. This variation is nearly 5% and it is necessary to work with a constant primary current if any consistency is to be expected in the observed value of i_s/i_p. This point seems to have been lost sight of by a large number of workers in the field of secondary emission.

(*a*) *Total secondary electron curve.*—Fig. 3 shows the graph between the ratio of the secondary current (i_s) to the primary current (i_p) and the applied potential.

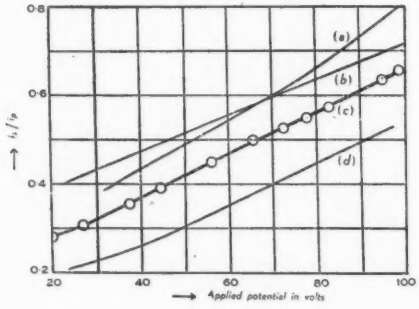


FIG. 3

(*a*) Warnecke (1936); (*b*) Petry (1925); (*c*) Author; (*d*) Rao (1930).

The results obtained by other investigators in the same region are also given in the same figure. It will be observed that while the absolute values differ from those of other workers, the general nature of the alteration with applied potential remains the same in all cases. The values obtained here lie between those of Petry and Rao.

(*b*) *Secondary emission at differnt temperatures of the target.*—Fig. 4 shows the values of i_s/i_p at temperatures between 30° and 500° at applied potentials of 66, 88 and 115 volts. Measurements were made both at

increasing and at decreasing temperatures of the target. It is found that in each case, the value of i_s/i_p is constant to within 1%.

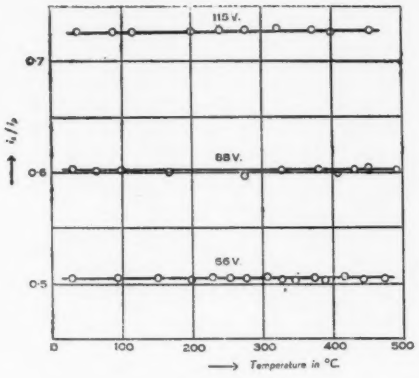


FIG. 4

Hayakawa (1933) found that at an applied potential of 71 volts, the secondary electron emission (he does not state what exactly this term means) rose from about 0·48 at 270° to about 0·6 at 365° (the Curie point) and thereafter to 0·75 at 420°. Similar changes were observed at an applied potential of 87 volts.

Tartakowsky and Kudrjawzewa (1932) found that at an applied potential of about 30 volts, the secondary emission showed a continued increase when the temperature of the metal was raised from 150°–350° C. An abrupt fall occurred at the Curie point (358° C.) and thereafter there was a rapid rise till 445° C. was reached.

Treloar and Landon (1938) found that in the range 100°–525° and at applied potentials of 30, 40, 50, 70 and 100 volts, the secondary emission coefficient showed a slight and gradual decrease as the temperature was raised. They attribute this decrease to the possible adsorption of gas by the metal surface when it was gradually cooled.

The present investigation shows that the coefficient is constant to within 1% in the temperature range 30°–500° C.

(*c*) *Influence of stray magnetic fields.*—A careful examination was made of the influence of stray magnetic fields on the value of the secondary electron emission coefficient in any setting. The magnetic field was produced by keeping near the experimental pyrex tube, one or more large bar magnets. The currents read in the primary and secondary galvanometers did not show

any variation. It may be safely concluded that stray magnetic fileds could in no way influence the value of the secondary coefficient.

Greater interest perhaps attaches to experiments conducted with the filament taking the position shown in Figs. 5*a* and 5*b*. In the first case, there were six turns of tungsten wire, each turn having a diameter of about

FIG. 5

4 mm. An approximate calculation showed that the intensity of the magnetic field on the axis of the coil and in the region occupied by the nickel target was of the order 5 gauss. In the second position of the filament, the magnetic field at the same place acts parallel to the axis of the coil and has an intensity which is nearly half this value. But in both the cases the secondary emission had the same coefficient showing that variations of the magnetic field of this order had no effect.

4. *Discussion*

It appears to the present writer that there is a fundamental theoretical difficulty in the conclusions of Hayakawa (1933). He finds an opposite variation of the secondary electron current above and below a critical voltage, which in the case of nickel is 38 volts. When the incident electrons are accelerated at a potential less than 38 volts, the parts of the secondary electron curve just above and below the point make an angle between 90° and 180° on the side of the temperature axis. But at applied potentials above 38° this angle becomes greater than 180°.

Hayakawa postulates that at applied potentials less than the critical value, only the free electrons are emitted as the secondary electrons. But when the applied potential is greater than the critical value, the ' structure electrons ' (whose potential energy is larger than that of the free electrons) are involved in inelastic collisions and they are hence expelled as secondary electrons. Hence one would expect an additional secondary emission current as soon as the applied potential exceeds the critical value, but not any kind of opposite variation of the electron current above and below the critical voltage. Further if his reasoning is true, no sudden variation of the secondary emission would be observed at applied potentials less than 38 volts. The reasoning of Hayakawa will not explain the variation at the critical temperature.

Fig. 5 is inverted. Correct position is—

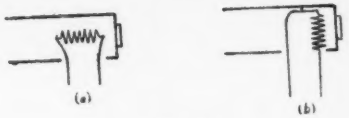


FIG. 5

A theory of secondary emission has recently been suggested by Woolridge (1939*a*). The production of secondary emission by the interaction of primary electrons with the valence electrons of a metal target was treated by him from the point of view of quantum mechanics. He has developed a method of calculating approximately the variation of the secondary coefficient with applied potential. His expression involves among other factors, the lattice spacing, the mean Fermi energy of the metal and the work function. None of these quantities may be said to vary abruptly at the Curie temperature. Woolridge has verified his deductions with the experimental results of Bruining and de Boer (1938) and of his own investigations on cobalt and nickel (Woolridge, 1939*b*). There seems to be theoretical justification for the conclusion that the secondary coefficient does not show any sudden change at the Curie temperature.

These considerations receive considerable weight from the experimental work of Rao (1930) to which attention has already been drawn. No anomalies were observed by him in the photoelectric and soft X-ray excitation curves at the Curie temperature. Richardson (1930) has shown that the second group of electrons returned with an energy just lower than the energy of the primary electrons is responsible for the emission of low energy electrons and excitation of soft X-rays. A change in the number of the former at the Curie temperature should be accompanied (most likely) by a change in the latter case.

Attention has already been drawn to the observation of Tartakowsky and Kudrjawzewa (1932) to the steady increase in the secondary coefficient of copper as its temperature was increased from 260°–390°. The secondary emission in arbitrary units rose from 46·5 to 54 in this range. This seems most improbable in the light of the foregoing discussion. Krefft (1928) who worked with tungsten found no change in the secondary coefficient when the temperature was raised to about 1450° C.

5. *Summary*

A study of the secondary electron emision from nickel has been made at different temperatures ranging from 30°–470° C. at certain definite applied potentials. No sudden alteration in the secondary electron current was observed at the Curie point (358° C.). These results are at variance with those of Tartakowsky and Kudrjawzewa and of Hayakawa. Attention is drawn to the investigations of Rao wherein no abrupt variations were obtained in the photoelectric emission and soft X-ray excitation curves of nickel at the Curie point. It is difficult to understand how in such closely connected phenomena, anomalies exist in one class and not in the other.

Support from this point of view is adduced for the conclusions of this investigation.

I take this opportunity of expressing my grateful thanks to Dr. S. Ramachandra Rao for his interest in the work.

REFERENCES

Bruining and Boer	..	*Physica*, 1938, **5**, 17.
Hayakawa	..	*Sci. Rep. Tohoku Univ.*, 1933, **22**, 934.
Krefft	..	*Phys. Rev.*, 1928, **31**, 199.
Petry	..	*Ibid.*, 1925, **26**, 346.
Rao	..	*Proc. Roy. Soc.*, (A), 1930, **128**, 41, 57.
————	..	*Ibid.*, 1933, **139**, 436.
————	..	*Ibid.*, 1937, **159**, 283.
Richardson	..	*Ibid.*, 1930, **128**, 63.
Rudberg	..	*Ibid.*, 1930, **127**, 111.
Tartakowsky and Kudrjawzewa		*Z. Phys.*, 1932, **75**, 137.
Treloar and Landon	..	*Proc. Phys. Soc.*, 1938, **50**, 625.
Warnecke	..	*Jour. de Phys.*, 1936, **7**, 270.
Woolridge	..	*Phys. Rev.*, 1939*a*, **56**, 562.
————	..	*Ibid.*, 1939*b*, **56**, 1063.

STUDIES IN THE FRIEDEL-CRAFTS REACTION

Part VI. Further Evidence for γ-Substitution in the Resorcinol and Orcinol Derivatives

By R. D. Desai and (Miss) V. M. Vakil

(From the Department of Chemistry, St. Xavier's College, Bombay)

Received September 2, 1940

In continuation of the work published by Desai and Ekhlas[1] in Part IV of this series, we have extended the action of acetic anhydride and benzoyl chloride on resacetophenone, β-orcacetophenone and 4-benzoylresorcinol. We have also repeated the action of acetyl chloride on orcinol and find that a mixture of β- and γ-orcacetophenones (I) is obtained, and that no trace of the 5-hydroxy 4 : 7-dimethylcoumarin which was noticed by us before (*loc. cit.*) is formed. However, our present result does not contradict our previous observation as γ-orcacetophenone must be the progenitor of 5-hydroxy-4 : 7-dimethylcoumarin. Though the yield of γ-orcacetophenone varies from 20–25 per cent., this method is much preferable to that of Rasinski.[2] It is curious that when acetic anhydride is substituted for acetyl chloride the yield of the γ-orcacetophenone is almost negligible. Similarly benzoyl chloride and orcinol gave only the β-substitution as 2 : 4- dihydroxy-6-methylbenzophenone (II) was the sole product of the reaction.

As the hitherto inaccessible γ-orcacetophenone was on hand, we have prepared its oxime, and *p*-nitrophenylhydrazone, and reduced it to 2-ethyl-5-methylresorcinol by Clemmensen's method. Its Pechmann Condensation as well as the Kostanecki Reaction has been described in a separate communication as they are sufficiently interesting.

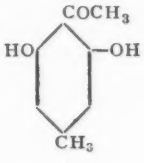
β-Orcacetophenone and acetic anhydride gave exclusively the γ-substitution as the only product formed was 2 : 4-diacetyl-5-methylresorcinol (III), the constitution of which followed from the fact that the same product was obtained by the action of acetic anhydride on γ-orcacetophenone.

Benzoyl chloride reacted with resacetophenone giving the γ-substitution as 2-benzoyl-4-acetylresorcinol (IV) and the 4-O-benzoyl derivative (V) of resacetophenone were only formed. The constitution of (IV) was proved by its rational synthesis from benzoyl chloride and methyl 2 : 4-dihydroxy-5-acetyl benzoate (VI) the preparation as well as orientation of which has already been described by Desai and Ekhlas (*loc. cit.*). A good yield of

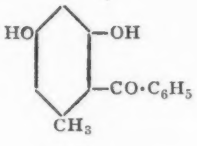
methyl 2 : 4-dihydroxy-3-benzoyl-5-acetyl benzoate (VII) was formed, and its free acid underwent decarboxylation smoothly giving the ketone (IV). When the 4-0-benzoyl derivative of resacetophenone was heated with anhydrous aluminium chloride it was converted into 2-benzoyl-4-acetylresorcinol (IV). Our attempts to synthesise the ketone (IV) by the action of acetic anhydride on 2-benzoylresorcinol (Friedel-Crafts method) under various conditions failed.

Acetic anhydride reacted with 4-benzoyl resorcinol giving 2-acetyl-4-benzoyl resorcinol (γ-substitution) and 2 : 6-diacetyl-4-benzoyl-resorcinol (VIII). 2-Acetyl-4-benzoyl resorcinol was also synthesised from 2-acetyl-resorcinol and benzoyl chloride, while the ketone (VIII) was also obtained from 2-acetyl-4-benzoylresorcinol and acetic anhydride. Benzoyl chloride as well as benzoic anhydride reacted with 4-benzoylresorcinol, but our attempts to insolate crystalline products from the resulting gums proved abortive.

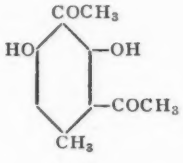
Thus it follows from the above results that orcinol, resacetophenone, β-orcacetophenone, and 4-benzoylresorcinol give the γ-substitution products when acted upon by acetyl chloride or acetic anhydride in the presence of anhydrous aluminium chloride. The only positive case of γ-substitution using benzoyl chloride or benzoic anhydride is that of resacetophenone, as our experiments with 4-benzoylresorcinol are not conclusive.



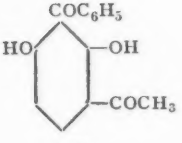
(I)



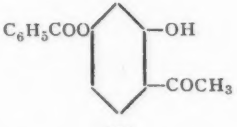
(II)



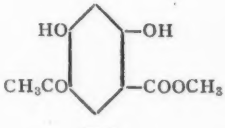
(III)



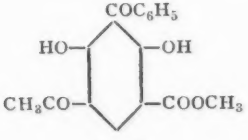
(IV)



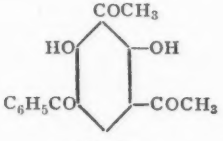
(V)



(VI)



(VII)



(VIII)

Experimental

(*A*) *Action of acetyl chloride on orcinol and isolation of γ-orcacetophenone or* (2 : 6-*dihydroxy*-4-*methylacetophenone*).

After anhydrous orcinol (12 g.) was dissolved in a solution of anhydrous aluminium chloride (26 g.) in dry nitrobenzene (150 c.c.), acetyl chloride (20 c.c.) was gradually added, and the mixture warmed on water-bath under reflux for two hours after keeping at the room temperature for 24 hours. Having decomposed the aluminium chloride with ice-cold dilute HCl, the nitro-benzene was removed in steam, and the solid that separated out on keeping the cold mixture was filtered off. This was recrystallised from hot water, when white needles, m.p. 142–44°, separated out. This product was identified as γ-orcacetophenone (yield 8 g.) by comparison with an authentic specimen prepared by Rasinski's method.

N.B.—A series of seven experiments was carried out. γ-Orcacetophenone was exclusively formed in four of them in yields varying from 20–25 per cent. In the case of other three experiments, a mixture of β- and γ-orcacetophenones was formed. This was separated by means of benzene, when the first fraction, m.p. 159–60°, always consisted of the β-variety, while the γ-isomer crystallised out subsequently. Finally an inseparable mixture of both the ketones used to remain. We are not in a position to explain why different experiments behave in a slightly different manner.

The oxime was prepared by heating an alcoholic solution of the ketone (0·5 g.), hydroxylamine hydrochloride (0·2 g.) and 5 per cent. NaOH (3 c.c.) under reflux for four hours, and acidifying the solution with hydrochloric acid. It crystallised from alcohol in tiny needles, m.p. 211–12°. (Found: N, 7·7; $C_9H_{11}O_3N$ requires N, 7·7 per cent.)

The p-nitrophenylhydrazone was prepared by heating under reflux the alcoholic solution of the ketone (0·5 g.) and *p*-nitrophenylhydrazine for six hours, and crystallising the resulting product from alcohol when red, microcrystalline plates, m.p. 245°, were obtained. (Found: N, 13·6; $C_{14}H_{12}O_4N_3$ requires N, 13·9 per cent.)

Reduction to 2-*ethyl*-5-*methylresorcinol*.—A mixture of zinc amalgam (10 g.), the ketone (1 g.) and dilute HCl (25 c.c.) was heated on sand-bath under reflux for four hours. The cooled solution was saturated with salt and extracted with ether, dried, and the solvent recovered. The residue crystallised from hexane in white needles, m.p. 135° (mixed m.p. with the original ketone was 95–97°). (Found: C, 71·3; H, 7·9; $C_9H_{12}O_2$ requires C, 71·1; H, 7·9 per cent.)

Action of benzoyl chloride on orcinol and formation of 2: 4-*dihydroxy*-5-*methylbenzophenone* (*II*).—To a solution of anhydrous aluminium chloride (14 g.) in nitrobenzene (75 c.c.), dry orcinol (12 g.) and benzoyl chloride (17 g.) were alternately added; the mixture was heated for one hour on the water-bath after allowing it to remain overnight, and worked up as usual. The sticky solid, purified through alkali was first triturated with sodium bicarbonate solution to get rid of benzoic acid, and crystallised from benzene when pale-yellow needles, m.p. 138°, were obtained. These were identified as 2: 4-dihydroxy-5-methylbenzophenone by comparing it with an authentic specimen prepared by Hoesch's method.[3]

(*B*) *Condensation of acetic anhydride with* β- *and* γ-*orcacetophenones and formation of* 2: 4-*diacetyl*-5-*methylresorcinol* (*III*).

The condensation was carried out as usual using the ketone (2 g.) anhydrous aluminium chloride (3·5 g.), acetic anhydride (1·5 g.) and nitrobenzene (50 c.c.). The mixture was worked up after heating on water-bath for six hours. The brownish solid obtained by ether extraction was purified through alkali and crystallised from hot water when lustrous needles, m.p. 95°, were obtained. Its alcoholic solution gave a purple-red coloration with ferric chloride (yield 15–20 per cent.). (Found: C, 63·6; H, 5·8; $C_{11}H_{12}O_4$ requires C, 63·5; H, 5·8 per cent.)

β- as well γ-orcacetophenones gave the same product as shown by mixed m.p.

The p-nitrophenylhydrazone prepared as usual crystallised from much alcohol in red, micro-crystalline needles, m.p. 242°. It gave high values for nitrogen showing that it was a mixture of mono-nitro- and dinitro-phenylhydrazones. (Found: N, 14·1; $C_{17}H_{17}O_5N_3$ requires N, 12·2 per cent., while $C_{23}H_{22}O_6N_6$ requires N, 17·6 per cent.)

(*C*) *Condensation of benzoyl chloride with resacetophenone, formation of* 2-*benzoyl*-4-*acetyl-resorcinol* (*IV*) *and* 4-*O*-*benzoyl-resacetophenone* (*V*).

This was carried out as usual using benzoyl chloride (24 g.), resacetophenone (20 g.), aluminium chloride (18 g.) and nitrobenzene (200 c.c.) and heating on water-bath for two hours. On working up the reaction product, the viscous, brown oil that was obtained was first treated with a solution of sodium bicarbonate to remove benzoic acid, and then dissolved in 5 per cent. caustic soda solution. The solid obtained on acidification was dried, and exhaustively extracted with petroleum ether (b.p. 60–80°), which dissolved a considerable portion. The insoluble residue was alternately crystallised from benzene and alcohol when 2-*benzoyl*-4-*acetyl resorcinol* was obtained

as pale-yellow, lustrous needles, m.p. 165° (yield 0·8 g.). (Found: C, 70·6; H, 4·8; $C_{15}H_{12}O_4$ requires C, 70·3; H, 4·7 per cent.)

Its alcoholic solution gave red coloration with ferric chloride solution. It could not be brominated at the ordinary temperature either in chloroform or glacial acetic acid solution. Similarly, it could not be condensed with acetic anhydride in presence of anhydrous aluminium chloride.

The p-nitrophenylhydrazone crystallised from alcohol as a red microcrystalline powder which did not melt upto 300°. (Found: N, 10·4; $C_{21}H_{17}O_5N_3$ requires N, 10·7 per cent.)

The petroleum ether solution gave a solid which crystallised from alcohol in lustrous plates, m.p. 110°, and was identified as 4-O-benzoylresacetophenone as it was hydrolysed by alkali to benzoic acid and resacetophenone (yield 7·2 g.). (Found: C, 70·4; H, 4·8; Calc. for $C_{15}H_{12}O_4$: C, 70·3; H, 4·7 per cent.)

Baker[4] who has prepared this compound by the benzoylation of resacetophenone gives the m.p. 106–07°.

The mono-bromo-derivative crystallised from alcohol in white, lustrous needles, m.p. 176°. (Found: Br, 23·7; $C_{15}H_{11}O_4Br$ requires Br, 23·9 per cent.)

Fries transformation of 4-*O-benzoylresacetophenone*.—An intimate mixture of the ketone (2 g.) and anhydrous aluminium chloride (4 g.) was heated in an oil-bath at 140° for one-and-half hours. The solid obtained by decomposing the aluminium chloride with ice-cold hydrochloric acid was purified through alkali, and extracted with hexane. The hexane-insoluble portion crystallised from alcohol in pale-yellow needles, m.p. 164–65°, and was identical with 2-*benzoyl*-4-*acetylresorcinol* described before (yield 15 per cent.). The hexane-soluble portion was the original unchanged material, m.p. 110°.

Synthesis of 2-*benzoyl*-4-*acetylresorcinol from benzoyl chloride and methyl* 2:4-*dihydroxy*-5-*acetyl benzoate* (*VI*).—To a solution of methyl 2:4-dihydroxy-5-acetylbenzoate (2 g.) and anhydrous aluminium chloride (1·6 g.) in nitro-benzene (50 c.c.), benzoyl chloride (1·7 g.) was gradually added with constant shaking, and the mixture was heated in an oil-bath at 130–40° for six hours after allowing it to remain at the room temperature overnight. After the decomposition of aluminium chloride with ice-cold HCl and removal of the nitrobenzene in steam, an oil which solidified immediately was left. This was filtered off, and the solid was triturated with a dilute solution of sodium bicarbonate. The residue crystallised from alcohol in colourless needles, m.p. 204°. This was *methyl* 2:4-*dihydroxy*-3-*benzoyl*-5-*acetylbenzoate*

(*VII*) and its alcoholic solution gave a red coloration with ferric chloride (yield 42 per cent.). (Found: C, 64·7; H, 4·6; $C_{17}H_{14}O_6$ requires C, 65·0; H, 4·5 per cent.)

The sodium bicarbonate solution, on acidification, gave an acid which is described below.

Hydrolysis of methyl 2: 4-*dihydroxy*-3-*benzoyl*-5-*acetylbenzoate to* 2: 4-*dihydroxy*-3-*benzoyl*-5-*acetylbenzoic acid.*—A solution of the above ester (1 g.) in 5 per cent. sodium hydroxide (30 c.c.) was heated on sand-bath under reflux for six hours and the cooled, filtered solution was acidified with concentrated HCl. The filtered solid was triturated with dilute solution of sodium bicarbonate when much of it dissolved. The residue crystallised from alcohol in pale-yellow needles, m.p. 165°, and was identified as 2-benzoyl-4-acetylresorcinol. The sodium bicarbonate solution gave 2: 4-*dihydroxy*-3-*benzoyl*-5-*acetylbenzoic acid* on acidification with concentrated HCl, and crystallised from dilute alcohol in needles, m.p. 217°. Its alcoholic solution gave a red coloration with ferric chloride. (Found: C, 63·8; H, 4·1; $C_{16}H_{12}O_6$ requires C, 64·0; H, 4·0 per cent.)

When the above acid was heated in a test-tube at 220–25° for one hour, much carbon dioxide was evolved, and the residue, after the usual purification, crystallised from alcohol in pale-yellow needles, m.p. 165°. The m.p. was undepressed by admixture with a specimen of 2-benzoyl-4-acetylresorcinol obtained by the condensation of resacetophenone with benzoyl chloride.

(*D*) *Condensation of acetic anhydride with* 4-*benzoylresorcinol and isolation of* 2-*acetyl*-4-*benzoylresorcinol and* 2: 6-*diacetyl*-4-*benzoylresorcinol* (*VIII*).

A mixture of anhydrous aluminium chloride (10 g.), 4-benzoylresorcinol (7 g.), acetic anhydride (4 g.) and nitrobenzene (75 c.c.) was heated on a water-bath for six hours. The product isolated in the usual manner was purified through 5 per cent. NaOH, and the crude solid (m.p. 80–85°) was exhaustively treated with petrol (b.p. 60–80°) till the m.p. of the insoluble residue rose to about 135°. The petrol solution, on concentration, gave a solid which crystallised from dilute alcohol in colourless needles, m.p. 107–08°, and was identified as 2-*acetyl*-4-*benzoylresorcinol* (yield 30 per cent.). Its alcoholic solution gave a wine-red coloration with ferric chloride. (Found: C, 70·4; H, 4·7; $C_{15}H_{12}O_4$ requires C, 70·3; H, 4·7 per cent.)

The p-nitrophenylhydrazone was a red, micro-crystalline powder, m.p. 227–29°, and sparingly soluble in alcohol. (Found: N, 9·9; $C_{21}H_{17}O_5N_3 + H_2O$ requires N, 10·3 per cent.)

The petrol-insoluble residue was recrystallised from dilute alcohol. The first fraction consisted of unchanged 4-benzoylresorcinol (m.p. 145°), while the second fraction melted at 151°, and this m.p. was unchanged by subsequent recrystallisation. Its alcoholic solution gave a cherry-red colour with ferric chloride and was identified as 2:6-*diacetyl*-4-*benzoylresorcinol* (yield 5 per cent.). (Found: C, 68·6; H, 4·8; $C_{17}H_{14}O_5$ requires C, 68·5; H, 4·7 per cent.)

The p-nitrophenylhydrazone was a reddish, micro-crystalline powder almost insoluble in alcohol and melted at 288–90° (Dec.). (Found: N, 9·6; $C_{23}H_{19}O_6N_3$ requires N, 9·7 per cent.)

Synthesis of 2-acetyl-4-benzoylresorcinol from 2-acetylresorcinol and benzoyl chloride.—The 2-acetylresorcinol required for this condensation was prepared by the method of Limaye.[5]

A solution of 2-acetylresorcinol (1 g.), aluminium chloride (1 g.), and benzoyl chloride (1·2 g.) in nitrobenzene (30 c.c.) was kept at the ordinary temperature, and then heated on water-bath for one hour. After working up the mixture in the usual manner, the viscous oil that was formed was first purified through dilute sodium bicarbonate solution. The insoluble residue (m.p. 70–75°) was extracted with petrol (b.p. 60–80°) which dissolved most of the solid leaving a viscous residue. The petrol solution, on concentration gave a solid (m.p. 94–100°) which crystallised from alcohol in needles, m.p. 108°. Its m.p. was not depressed by the product, m.p. 108°, isolated during the condensation of 4-benzoylresorcinol with acetic anhydride. When 2-acetyl-4-benzoylresorcinol was further condensed with acetic anhydride (Friedel-Crafts) the resulting product melted at 151°, and was identical with the other product obtained during the condensation of acetic anhydride with 4-benzoylresorcinol.

We take this opportunity to thank Prof. R. N. Bhagwat, M.A., B.SC., and Rev. Father G. Palacios, S.J., PH.D., D.D., for their kind interest in this work and provision of the facilities.

Summary

Definite and conclusive evidence of simultaneous β- and γ-substitution or γ-substitution alone has been obtained in the case of the reactions between (1) orcinol and acetyl chloride; (2) β-orcacetophenone and acetic anhydride; (3) benzoyl chloride and resacetophenone; and (4) acetic anhydride and 4-benzoylresorcinol in presence of anhydrous $AlCl_3$. The constitution of the resulting products have been established by their independent and rational synthesis.

REFERENCES

1. Desai and Ekhlas .. *Proc. Ind. Acad. Sci.*, (A), 1938, **8**, 194.
2. Rasinski .. *J. Pr. Chem.*, (2), **26**, 59.
3. Hoesch .. *Ber.*, 1915, **48**, 1130.
4. Baker .. *J.*, 1933, 1384.
5. Limaye .. *Rasayanam*, 1936, **1**, 66.

ON THE EXISTENCE OF A METRIC FOR PATH-SPACES OF ORDER TWO[1]

By V. Seetharaman

(From the Department of Mathematics, Annamalai University, Annamalainagar)

Received July 16, 1940

(Communicated by Prof. A. Narasinga Rao, Annamalainagar)

It is the purpose of this note to examine when we can identify the paths

$$x^{(3)i} + \alpha^i (x, x', x'', t) = 0$$

with the extremals of a regular problem of the calculus of variations. It is a known result that if $H_i = 0$ be the extremals of $\delta \int f dt = 0$, then, the equations of variation of $H_i = 0$ are self-adjoint. Here, we are attempting to prove the sufficiency of this condition.

It has been established[2] for equations of order 2, *viz.*, $x^{(2)i} + \alpha^i (x, x', t) = 0$, that self-adjoincy of the equations of variation is necessary as well as sufficient for a metric to exist. While trying to extend this result for equations of Higher Order, we examine as a first step, the differential equations of order 3.

The given path-equations are contravariant whereas, the equations of the calculus of variation will be covariant. If we are to identify the two, we should necessarily have a tensor of association. Kosambi[3] has shown that the very term self-adjoincy implies the existence of such a tensor, as the equations of variation are contravariant while their adjoint will be covariant. He has also established that a convenient means of association is by a covariant tensor f_{ij} of rank 2. Hence we have that

$$H_i (x, x', x'', x''', t) = f_{ij} \{x^{(3)j} + \alpha^j\}.$$

It is shown later that this is a consequence of the self-adjoincy conditions.

In Art. 1, we analyse the self-adjoincy conditions. We deduce that f_{ij} is an anti-symmetric tensor which is a curl and hence

$$f_{ij} = \phi_{i\,;\,j} - \phi_{j\,;\,i}.$$

---

[1] I express my thanks to Prof. D. D. Kosambi for his kind guidance and helpful suggestions.

[2] D. R. Davis, "The Inverse Problem of the Calculus of Variations in a Space of $(n + 1)$ Dimensions," *Bull. American Math. Soc.*, 1929, 371–80.

D. D. Kosambi, *Quart. J. of Math.* (*Oxford*), 1935, **6**, 9.

[3] D. D. Kosambi, *loc. cit.*, p. 5.

The metric that is sought must be of the form $f = \phi_r \ddot{x}^r + \psi$, ϕ_i and ψ being functions of x, x' and t. For, the most general $f(x, x', x'', t)$ will yield equations of the 4th order, whereas the given path-equations are of the 3rd order. So, the coefficient of $x^{(4)i}$, *viz.*, $J_{(2)i\,(2)j} = 0$ which gives us $f = \phi_r \ddot{x}^r + \psi$. This ϕ_i is precisely the one in J_{ij} and is determined to within a function whose curl vanishes. Since the addition of this to f, amounts to adding a perfect differential, we ignore its effect. So we take it that a ϕ_i is known and a ψ has to be determined, so that

$$\delta_i (\phi_r \ddot{x}^r + \psi) = 0$$

or

$$E_i \equiv \delta_i (\phi_r \ddot{x}^r) = -\delta_i \psi.$$

Two interpretations are here possible. First, we can regard this as a differential system for the unknown ψ in terms of the known ϕ_i. In Art. 2, five necessary conditions of integrability of this differential system are deduced. The first three suffice to say that

$$E_i = \psi_{;\,i\,;\,k} \ddot{x}^k + A_i (x, x', t)$$

and from the latter two we have to specify the particular form of A_i. It is not obvious if they are sufficient to do so. Let us turn to the second point of view. The system E_i must be identified with $\delta_i (-\psi)$, *i.e.*, with the Euler equations of minimising $\int -\psi (x, x', t)\, dt$. The necessary and sufficient condition for this is that the equations of variation of E_i should form a self-adjoint system. It is seen that the five integrability conditions deduced above, are precisely the conditions of self-adjoincy of the variation of E_i.

In Art. 3, we show that the integrability conditions deduced in Art. 2 are satisfied in virtue of the self-adjoincy conditions deduced in Art. 1. In establishing this, we make use of the tensorial form of the Euler equations. The identities, besides those explicitly stated, of one of the author's previous papers,[4] are freely used. To some extent profitable use is made of normal co-ordinates, *i.e.*, one in which r^i_j, $Dr^i_j \cdots$ vanish along a path. The notations of the last paper are used except sometimes we write for convenience

$$\phi_{i\,|\,j} \quad \text{for} \quad \underset{0}{\nabla}_j \phi_i, \quad \phi_{i;\,j} \quad \text{for} \quad \underset{1}{\nabla}_j \phi_i, \quad \phi_{i,\,j} \quad \text{for} \quad \phi_{i(0)j}, \text{ etc.}$$

The above reasoning, in which the problem is reduced practically to the case $\sigma = 1$, is valid for the general σ and one can reasonably expect the result to hold good. But one experiences a practical difficulty in establishing that the corresponding integrability conditions are satisfied. From the very general character of σ, the process does not end in a definite number of steps.

[4] V. Seetharaman, *Proc. Ind. Acad. Sci.*, 1937, **5**, No. 2.

1. *Self-Adjoincy Conditions*

We use the Lemma[5] that

$$\underset{p}{A_{ij}}\, u^{(p)j} = 0 \quad (p = 0, 1, 2, 3)$$

will be self-adjoint, if and only if,

$$\underset{p}{A_{ij}} = \sum_{r=p}^{3} (-1)^r \binom{r}{p} \underset{r}{A_{ji}^{(r-p)}}.$$

Applying this to the equations of variation of $H_i(x, x', x'', x''', t) = 0$ we get,

$$\text{(A)}\quad H_{i(3)j} = -H_{j(3)i}$$

$$\text{(B)}\quad H_{i(2)j} = H_{j(2)i} - 3H^{(1)}_{j(3)i}$$

$$\text{(C)}\quad H_{i(1)j} = -H_{j(1)i} + 2H^{(1)}_{j(2)j} - 3H^{(2)}_{j(3)i}$$

$$\text{(D)}\quad H_{i(0)j} = H_{j(0)i} - H^{(1)}_{j(1)i} + H^{(2)}_{j(2)i} - H^{(3)}_{j(3)i}.$$

These should be identities in x, x', x'', etc.

In (B), the coefficient of $x^{(\nu)k}$, $\nu \geqslant 4$ is zero and hence we have

$$H_{j(3)i(\nu)k} = 0 \quad \nu \geqslant 3$$

i.e.,
$$H_{j(3)i} = f_{ji}\ (x, x', x'', t)$$

and hence
$$H_j = f_{ji}\ x^{(3)i} + M_j\ (x, x', x'', t). \tag{1·1}$$

So we have that the Euler equations should be linear in their highest derivatives, a result arrived at already.

Let us apply the above four conditions to this form of the Euler equations.

By (A) we have that

$$f_{ij} = -f_{ji} \tag{1·2}$$

(B) gives us

$$f_{ik(2)j}\, x^{(3)k} + M_{i(2)j} = f_{jk(2)i}\, x^{(3)k} + M_{j(2)i} - 3f^{(1)}_{ji}.$$

Equating the coefficient of $x^{(3)k}$ to zero, we have

$$f_{ik(2)j} - f_{jk(2)i} + 3f_{ji(2)k} = 0$$

i.e.,
$$f_{ik(2)j} + 3f_{ji(2)k} + f_{kj(2)i} = 0.$$

Two cyclic permutations of i, j, k and addition gives us

$$f_{ik(2)j} + f_{ji(2)k} + f_{kj(2)i} = 0$$

and hence
$$f_{ji(2)k} = 0. \tag{1·3}$$

---

[5] D. D. Kosambi, *Quart. J. of Math.*, 1936, 7, 103.

The residual terms in (B) are

$$M_{i(2)j} - M_{j(2)i} + 3 f^{(1)}_{ji} = 0$$

i.e.,

$$3 D f_{ji} = 0 \tag{1·4}$$

Evaluating (C), making use of (1·3), we have

$$f_{ik(1)j}\, x^{(3)k} + M_{i(1)j}$$

$$= - f_{jk(1)i}\, x^{(3)k} - M_{j(1)i} + 2 [M_{j(2)i}]^{(1)} - 3 f^{(2)}_{ji}.$$

Equating to zero, the coefficient of $x^{(3)k}$ in this we get,

$$f_{ik(1)j} + f_{jk(1)i} + 3 f_{ji(1)k} = 2 M_{j(2)i(2)k}.$$

Interchanging i and k and subtracting, we get

$$f_{ik(1)j} + f_{ji(1)k} + f_{kj(1)i} = 0 \tag{1·5}$$

(1·3), (1·2) and (1·5) taken all together imply[6] that f_{ij} is a curl;

i.e.,

$$f_{ij} = \phi_{i;j} - \phi_{j;i} \tag{1·6}$$

The other terms give

$$M_{i(1)j} + M_{j(1)i} - 2 M^{(1)}_{j(2)i} + 3 f^{(2)}_{ji} = 0$$

i.e.,

$$f_{ir}\, \alpha^r_{(1)j} + f_{jr}\, \alpha^r_{(1)i} - 2 [f_{jr}\, \alpha^r_{(2)i}]^{(1)} + 3 f^{(2)}_{ji} = 0.$$

Using normal co-ordinates, this is seen to be equivalent to

$$f_{ir} \underset{1}{P^r_j} + f_{jr} \underset{1}{P^r_i} + 3 D^2 f_{ji} = 0$$

and hence we get

$$f_{ir} \underset{1}{P^r_j} + f_{jr} \underset{1}{P^r_i} = 0. \tag{1·7}$$

Condition (D) reduces to

$$f_{ik(0)j}\, x^{(3)k} + M_{i(0)j}$$

$$= f_{jk(0)i}\, x^{(3)k} + M_{j(0)i} - [f_{jk(1)i}\, x^{(3)k} + M_{j(1)i}]^{(1)} + M^{(2)}_{j(2)i} - f^{(3)}_{ji}.$$

The coefficient of $x^{(4)k}$ in this equated to zero gives us

$$M_{j(2)i(2)k} = f_{jk(1)i} + f_{ji(1)k}. \tag{1·8}$$

Permuting (i, j, k) cyclically and adding, we get

$$M_{i(2)j(2)k} + M_{j(2)k(2)i} + M_{k(2)i(2)j} = 0$$

i.e.,

$$f_{ir}\, \gamma^r_{j(2)k} + f_{jr}\, \gamma^r_{k(2)i} + f_{kr}\, \gamma^r_{i(2)j} = 0. \tag{1·9}$$

From (1·8) it also follows that

$$M_{j(2)i(2)k(2)l} = 0$$

---

[6] A generalisation of Eisenhart's result and can be easily established by his own methods; *vide*, Eisenhart, *Bull. American Math. Soc.*, 1922, 28, 425–27.

and hence

$$a^i = A^i_{jk}(x, \dot{x}, t)\ \ddot{x}^j \ddot{x}^k + B^i_j(x, \dot{x}, t)\ddot{x}^j + C^i(x, \dot{x}, t) \qquad (1\cdot10)$$

The coefficient of $x^{(3)k}$ when equated to zero gives us

$$\left.\begin{aligned} &f_{jk,i} + f_{ki,j} + f_{ij,k} - f^{(1)}_{jk;i} - 3f^{(1)}_{ji;k} \\ &- M_{j(1)i(2)k} + M_{j(2)i(1)k} + 2\,M^{(1)}_{j(2)i(2)k} \end{aligned}\right\} = \text{zero.}$$

The use of normal co-ordinates and further simplification reduces this to

$$\begin{aligned} D f_{jk;i} = {} & f_{rj}(\underset{1}{\nabla}_k \gamma^r_i - \underset{1}{\nabla}_i \gamma^r_k) + 2 f_{ri}(\underset{1}{\nabla}_k \gamma^r_j - \underset{1}{\nabla}_j \gamma^r_k) \\ & + f_{rk}(\underset{1}{\nabla}_i \gamma^r_j - \underset{1}{\nabla}_j \gamma^r_i). \end{aligned} \qquad (1\cdot11)$$

We have

$$\begin{aligned} \underset{1}{\nabla}_i \gamma^r_k - \underset{1}{\nabla}_k \gamma^r_i &= \tfrac{1}{3} \underset{2}{\nabla}_k \underset{1}{P^r_i} + D\gamma^r_{k(2)i} \\ &= \tfrac{1}{6}(\underset{2}{\nabla}_k \underset{1}{P^r_i} - \underset{2}{\nabla}_i \underset{1}{P^r_k}). \end{aligned}$$

Using the first form for terms 1 and 3 and the other form for the second, we get

$$\begin{aligned} D f_{jk;i} = {} & \tfrac{1}{3} \underset{2}{\nabla}_k (f_{jr} \underset{1}{P^r_i} + f_{ir} \underset{1}{P^r_j}) \\ & + \tfrac{1}{3} \underset{2}{\nabla}_j (f_{rk} \underset{1}{P^r_i} + f_{ri} \underset{1}{P^r_k}) \\ & + f_{rk} D\gamma^r_{i(2)j} + f_{jr} D\gamma^r_{k(2)i} \end{aligned}$$

and using (1·7) this becomes

$$D f_{jk;i} = f_{rk} D\gamma^r_{i(2)j} + f_{jr} D\gamma^r_{k(2)i},$$

a result which can be deduced from (1·4). The other terms left over in (D) give us

$$M_{i(0)j} - M_{j(0)i} + M^{(1)}_{j(1)i} - M^{(2)}_{j(2)i} + f^{(3)}_{ji} = 0.$$

This reduces to

$$f_{ir} \underset{0}{P^r_j} - f_{jr} \underset{0}{P^r_i} + D[f_{jr} \underset{1}{P^r_i}] + D^3 f_{ji} = 0$$

and hence

$$f_{ir} \underset{0}{P^r_j} - f_{jr}(\underset{0}{P^r_i} - D\underset{1}{P^r_i}) = 0. \qquad (1\cdot12)$$

Besides the two classes, which Kosambi expected[7] the self-adjoincy conditions to fall into, *viz.*, (1) those that can be immediately guessed at from the existence of a variational principle such as (1·2), (1·3) and (1·6) and (ii) those that give the relations between the curvature tensors as (1·7) and (1·12), we get, on closer examination formula (1·8), from which could be deduced

[7] D. D. Kosambi, *Quart. J. of Math.* (*Oxford*), 1936, 7, 103.

a relation connecting $\gamma^{i}_{j(2)k}$ (*vide* 1·9) and also the structure of α^{i} (*vide* 1·10).

On direct evaluation of $\delta_i(\phi_r \ddot{x}^r + \psi)$ we get

$$(\phi_{i;r} - \phi_{r;i})\dddot{x}^r + (\phi_{i;r;j} - \phi_{r;i;j})\ddot{x}^r \ddot{x}^j$$
$$+ \ddot{x}^r \left[\phi_{r,i} + \phi_{i,i} + 2\frac{\partial}{\partial t}\phi_{i;r} - \psi_{;i;r} - \frac{\partial}{\partial t}\phi_{r;i}\right]$$
$$+ \dot{x}^j (2\phi_{i;r,j} - \phi_{r;i,j})$$
$$+ \left[\dot{x}^r \left(2\frac{\partial}{\partial t}\phi_{i,r} - \psi_{;i,r}\right) + \phi_{i,r,j}\dot{x}^r \dot{x}^j + \psi_{,i} - \frac{\partial}{\partial t}\psi_{;i} + \frac{\partial^2}{\partial t^2}\phi_i\right] = \text{zero.}$$

This is in fact, of the form

$$f_{ir}\dddot{x}^r + A_{irj}(x, \dot{x}, t)\ddot{x}^r \ddot{x}^j + B_{ir}(x, \dot{x}, t)\ddot{x}^r + C_i(x, \dot{x}, t) = \text{zero},$$

which confirms our result (1·10).

2. It has been observed that from the self-adjoincy conditions, a function ϕ_i is determined and the problem reduces to finding a function $\psi(x, x', t)$ such that

$$E_i \equiv \delta_i(\phi_r \ddot{x}^r) = -\delta_i \psi$$
$$= -\psi|_i + D\psi_{;i}.$$

Let us find the necessary conditions of integrability of this differential system.

It is easily seen that $E_{i(2)j} = \psi_{;i;j}$ and hence we get

I. $E_{i(2)j} = E_{j(2)i}$

II. $E_{i(2)j(2)k} = 0$

III. $\underset{1}{\nabla}_k \underset{2}{\nabla}_j E_i = \underset{1}{\nabla}_j \underset{2}{\nabla}_k E_i$.

Next we have that

$$\underset{1}{\nabla}_j E_i = -\underset{1}{\nabla}_j \psi|_i + \underset{1}{\nabla}_j (D\psi_{;i})$$
$$= (\psi_{;i|j} - \psi_{;j|i}) - \psi_{;r} \underset{21}{R^r_{ij}} + D\psi_{;i;j}$$

and hence

IV. $\underset{1}{\nabla}_j E_i + \underset{1}{\nabla}_i E_j = 2D \underset{2}{\nabla}_j E_i$.

Then

$$\underset{0}{\nabla}_j E_i = -\psi_{|i|j} + D\psi_{;i-|j} - \psi_{;i;r} \underset{1}{P^r_j}$$
$$- \tfrac{1}{3}\psi_{;r}(A^r_{ij} - \underset{1}{\nabla}_j \underset{1}{P^r_i})$$

which gives

$$\text{V.}\quad \underset{0}{\nabla}_j E_i - \underset{0}{\nabla}_i E_j = D \underset{1}{\nabla}_j E_i - D^2 \underset{2}{\nabla}_j E_i + \underset{21}{R^r_{ij}} E_r + \underset{1}{P^l_i} E_{j(2)l} - \underset{1}{P^l_j} E_{i(2)l}.$$

Turning to the second point of view, we require that E_i should have its equations of variation self-adjoint. The conditions are,

$$E_{i(2)j} = E_{j(2)i} \tag{2·1}$$

$$E_{i(1)j} = -E_{j(1)i} + 2E^{(1)}_{j(2)i} \tag{2·2}$$

$$E_{i(0)j} = E_{j(0)i} - E^{(1)}_{j(1)i} + E^{(2)}_{j(2)i} \tag{2·3}$$

On a closer examination of (2·2) we get

$$E_{j(2)i(2)k} = 0, \tag{2·4}$$

and hence $E_i = \psi_{ik}(x, x', t)\,\ddot{x}^k + A_i\ (x\,x'\,t)$. (2·1) gives us that $\psi_{ij} = \psi_{ji}$ and the coefficient of $\ddot{x}^k$ in (2·2) equated to zero gives us

$$\psi_{ik;j} + \psi_{jk;i} - 2\psi_{ji;k} = 0.$$

Interchanging i and k and subtracting from the above we get

$$\psi_{jk;i} = \psi_{ji;k}. \tag{2·5}$$

This, together with the symmetry of ψ_{ij} ensures that

$$\psi_{ij} = \psi_{i;j;}.$$

The self-adjoincy conditions (2·1) to (2·5) are exactly the five conditions of integrability got above and hence they are necessary and sufficient. We proceed to show that they are satisfied in virtue of the conditions deduced in Art. 1.

3. $\delta_i f \equiv \underset{0}{\nabla}_i f - D \underset{1}{\nabla}_i f + D^2 \underset{2}{\nabla}_i f + \underset{1}{P^l_i} \underset{2}{\nabla} f$. Making use of the identities in the present author's paper referred to and keeping in mind that $f = \phi_r \ddot{x}^r + \psi$, we get

$$\underset{2}{\nabla}_j \delta_i f = (\phi_{j\,i} + \phi_{i\,j}) + D(2\phi_{i;j} - \phi_{j;i}) + \phi_r (\underset{1}{\nabla}_i \gamma^r_j + \underset{1}{\nabla}_j \gamma^r_i) - \ddot{x}^r \phi_{r;\,i;\,j} + 2\gamma^r_j \phi_{r;i} + 2\gamma^r_i \phi_{r;j} - \psi_{i;\,i;\,j} \tag{3·1}$$

Now $E_i = \delta_i (\phi_r \ddot{x}^r)$.

Hence

$$(\underset{2}{\nabla}_j \mathrm{E}_i - \underset{2}{\nabla}_i \mathrm{E}_j) = 3\,\mathrm{D}\,(\phi_{i;\,j} - \phi_{j;\,i})$$
$$= 3\,\mathrm{D}\,f_{ij}$$
$$= \text{zero (by } 1\cdot4). \tag{3·2}$$

$$\underset{2}{\nabla}_k \underset{2}{\nabla}_j \mathrm{E}_i = \underset{2}{\nabla}_k \underset{0}{\nabla}_i \phi_j + \underset{2}{\nabla}_k \underset{0}{\nabla}_j \phi_i + \underset{2}{\nabla}_k \mathrm{D}\,(f_{ij} + \phi_{i;\,j})$$
$$+ \phi_r \left(\underset{2}{\nabla}_k \underset{1}{\nabla}_i \gamma^r_j + \underset{2}{\nabla}_k \underset{1}{\nabla}_j \gamma^r_i\right) - \phi_{k;\,i;\,j}$$
$$+ 2\phi_{r;\,i}\gamma^r_{j(2)\,k} + 2\phi_{r;\,j}\gamma^r_{i(2)\,k}.$$

$$\underset{2}{\nabla}_k \underset{0}{\nabla}_i \phi_j = -\phi_{j;\,r}\,\gamma^r_{i(2)\,k} - \phi_r \left(\underset{2}{\nabla}_k \underset{1}{\nabla}_i \gamma^r_j\right)$$

and

$$\underset{2}{\nabla}_k \mathrm{D}\,\phi_{i;\,j} = \phi_{i;\,j;\,k} - \phi_{r;\,j}\,\gamma^r_{i(2)k} - \phi_{i;\,r}\,\gamma^r_{j(2)k}.$$

Hence

$$\underset{2}{\nabla}_k \underset{2}{\nabla}_j \mathrm{E}_i = \underset{2}{\nabla}_k (\mathrm{D}\,f_{ij}) + \underset{2}{\nabla}_j (\mathrm{D}\,f_{ik})$$
$$+ (f_{ri}\,\gamma^r_{j(2)k} + f_{rj}\,\gamma^r_{i(2)k} + f_{rk}\,\gamma^r_{i(2)j}) \tag{3·3}$$
$$= \text{zero by } (1\cdot4) \text{ and } (1\cdot9).$$

$$(\underset{1}{\nabla}_k \underset{2}{\nabla}_j \mathrm{E}_i - \underset{1}{\nabla}_j \underset{2}{\nabla}_k \mathrm{E}_i)$$
$$= 2\,f_{ir}\left(\underset{1}{\nabla}_j \gamma^r_k - \underset{1}{\nabla}_k \gamma^r_j\right) + f_{jr}\left(\underset{1}{\nabla}_i \gamma^r_k - \underset{1}{\nabla}_k \gamma^r_i\right)$$
$$+ f_{kr}\left(\underset{1}{\nabla}_j \gamma^r_i - \underset{1}{\nabla}_i \gamma^r_j\right) + \underset{1}{\nabla}_i (\mathrm{D}\,f_{jk}) + \underset{1}{\nabla}_j (\mathrm{D}\,f_{ki}) + \underset{1}{\nabla}_k (\mathrm{D}\,f_{ij})$$
$$- \mathrm{D}\,f_{jk;\,i} \tag{3·4}$$
$$= \text{zero by } (1\cdot4) \text{ and } (1\cdot11).$$

$$(\underset{1}{\nabla}_j \mathrm{E}_i + \underset{1}{\nabla}_i \mathrm{E}_j) - 2\,\mathrm{D}\,\underset{2}{\nabla}_j \mathrm{E}_i$$
$$= 3\,\mathrm{D}^2 f_{ji} + (f_{ri}\,\underset{1}{\mathrm{P}}{}^r_j + f_{rj}\,\underset{1}{\mathrm{P}}{}^r_i) \tag{3·5}$$
$$= \text{zero by } (1\cdot4) \text{ and } (1\cdot7).$$

$$(\underset{0}{\nabla}_j \mathrm{E}_i - \underset{0}{\nabla}_i \mathrm{E}_j) - \mathrm{D}\,\underset{1}{\nabla}_j \mathrm{E}_i + \mathrm{D}^2\,\underset{2}{\nabla}_j \mathrm{E}_i - \underset{1}{\mathrm{P}}{}^r_i\,\mathrm{E}_{j(2)r} + \underset{1}{\mathrm{P}}{}^r_j\,\mathrm{E}_{i(2)r} - \underset{21}{\mathrm{R}}{}^r_{ij}\,\mathrm{E}_r$$
$$= \mathrm{D}^3 f_{ij} - \left[f_{ir}\,\underset{0}{\mathrm{P}}{}^r_j - f_{rj}\,(\mathrm{D}\,\underset{1}{\mathrm{P}}{}^r_i - \underset{0}{\mathrm{P}}{}^r_i)\right] + \mathrm{D}\left[f_{ir}\,\underset{1}{\mathrm{P}}{}^r_j + f_{jr}\,\underset{1}{\mathrm{P}}{}^r_i\right) + \underset{1}{\mathrm{P}}{}^r_i (\mathrm{D}\,f_{rj})$$
$$= \text{zero by } (1\cdot4), (1\cdot7) \text{ and } (1\cdot12).$$

Hence we have established that a metric exists for path-spaces of order 2, if the equations of variation of the paths are self-adjoint.

ON A TABLE OF VALUES OF L (n)

By Hansraj Gupta

(*Department of Mathematics, Government College, Hoshiarpur*)

Received September 11, 1940

(Communicated by Dr. B. L. Bhatia, D.Sc., F.N.I.)

1. In what follows, all small letters denote integers $\geqslant 0$, p denoting a prime $\geqslant 2$.

We define $\lambda(n)$ by the relations:

$$\lambda(n) = -\lambda(n/p) \text{ where } p \mid n; \text{ and } \lambda(1) = 1. \tag{1}$$

Thus $$\lambda(475) = -\lambda(95) = \lambda(19) = -\lambda(1) = -1.$$

The function L (n) is now defined by the relation:

$$\mathrm{L}(n) = \sum_{m=1}^{n} \lambda(m). \tag{2}$$

At the suggestion of Dr. Chowla, I have recently calculated a table[1] which gives the values of L (n) for values of n up to 20,000. Every composite $n \leqslant 20{,}000$ is first of all broken into two factors one of these being the least prime that divides n. $\lambda(n)$ is then given immediately by (1). Thus when $\lambda(n)$ and L (n) have been calculated for every value of n up to 474, we have

$$\lambda(475) = \lambda(5 \cdot 95) = -1, \text{ because } \lambda(95) = 1.$$

Moreover
$$\mathrm{L}(475) = \lambda(475) + \mathrm{L}(474),$$
$$= -1 - 22 = -23.$$

I find that[2]

$$\mathrm{L}(n) \leqslant 0 \text{ for } 2 \leqslant n \leqslant 20{,}000. \tag{3}$$

Most probably L (n) is negative or zero for all $n \geqslant 2$.

2. Let s be the greatest value of $n \leqslant 20{,}000$, for which

$$\mathrm{L}(n) = -t.$$

---

[1] The work has been carefully checked with the help of some of my students—Satnam Singh in particular.

[2] Polya verified this for values of n up to 1000.

See Jahresberichte der deutsche Mathematiker Vereinigung, 1919.

Then the following table gives the values of s for values of t upto 10:

t ..	0	1	2	3	4	5	6	7	8	9	10
s ..	586	591	592	1411	1422	1425	1432	3281	3296	5645	19680

3. Let h be the least value of n for which $L(n) = -k$. Then the following table gives the values of h for values of k upto 150:—

k	0	1	2	3	4	5	6	7	8	9
	2	3	8	13	20	31	32	53	76	79
1	80	117	176	181	182	193	200	283	284	285
2	286	293	440	443	468	661	678	683	684	1075
3	1076	1087	1088	1091	1092	1093	1106	1109	1128	1129
4	1130	1131	1132	1637	1638	1753	1756	1759	1760	2699
5	2700	2703	2712	2713	2714	2715	2720	2731	2732	2739
6	2742	2769	2770	2801	2802	2803	2804	4157	4256	4261
7	4364	4373	4526	4527	4528	6317	6318	6381	6390	6391
8	6392	6397	6398	6399	6480	6481	6482	6575	6582	6859
9	6864	6877	6878	6969	6972	6975	6976	6977	6978	6987
10	6988	6997	7026	7027	9686	9689	9690	9695	9696	9697
11	9698	9699	9700	9719	9720	9721	9724	9725	9726	9789
12	9792	9795	9816	9817	9822	9823	9836	9837	9840	15669
13	15670	15671	15672	15675	15676	15679	15680	15745	15750	15753
14	15756	15791	15792	15795	15798	15799	15804	15805	15806	15807
15	15810	> 20000								

Within the limits of my table, $\{L(n)\}^2/n$ is the greatest for $n = 9840$. For this value of n, $\{L(n)\}^2/n$ is just $< \frac{5}{3}$. It thus appears that

$$|L(n)| = O(\sqrt{n}). \tag{4}$$

4. The following table will show the main variations in the value of $L(n)$ as n increases from 2 to 20,000.

n	L (n)	n	L (n)
2	0	3281	− 7
468	− 24	4528	− 74
586	0	5645	− 9
684	− 28	7027	− 103
880	− 6	8512	− 14
1132	− 42	9840	− 128
1411	− 3	12798	− 32
1760	− 48	15810	− 150
2264	− 8	19680	− 10
2804	− 66		

SELENIUM IODIDE

By M. R. Aswatha Narayana Rao

Department of Chemistry, University of Mysore, Central College, Bangalore

Received July 24, 1940

(Communicated by Prof. B. Sanjiva Rao)

Introduction

Ever since the discovery of selenium by Berzelius[1] attempts have been made to prepare the iodide of the element. Schneider[2] believed that the iodide could be prepared by fusing together the two elements or by the reaction of selenium bromide with ethyl iodide. Guyot[3] stated that the two elements combined in carbon disulphide solution. But investigations on the freezing point curves of binary mixtures of the two elements by Pellini and Pedrina[4] showed that no compound was produced. Olivari[5] and Beckmann and co-workers[6–9] determined the molecular weight of selenium using iodine, as the cryoscopic solvent. They also used as solvent methylene iodide containing dissolved iodine. They could not obtain any evidence for the existence of selenium iodide. Wright[10] arrived at similar conclusions by his studies on the partial pressures of iodine in equilibrium with fused mixtures of selenium and iodine. Recently, the colour change produced by the addition of selenium to a solution of iodine in carbon tetrachloride, was attributed by McCullough[11] to the formation of selenium iodide in the solvent.

The present author showed that sulphur iodide[12] and thionyl iodide[13] were produced when dilute solutions of the respective chlorides in carbon tetrachloride, were treated with potassium iodide. In this investigation an attempt was made to prepare selenium iodide by employing the same technique. When a dilute solution of selenium monochloride in carbon tetrachloride was shaken up with dry potassium iodide powder, the solution turned yellow in colour; the yellow colour changed to violet within a few seconds of exposure to light; at the same time, tiny crystals of selenium separated from the solution. The yellow colour was suspected to be due to the presence of selenium mono-iodide and a detailed investigation was undertaken.

Experimental

Reagents used.—(1) Carbon tetrachloride: Merck's "Pure" carbon tetrachloride was dried over phosphorus pentoxide and distilled. (2) Potassium iodide: Potassium iodide (Merck's "extra pure") was finely powdered

and dried over phosphorus pentoxide for 24 hours in a vacuum desiccator. (3) Selenium monochloride: Lenher's[14] method was employed to prepare selenium monochloride. Dry chlorine was passed through excess of red amorphous selenium suspended in carbon tetrachloride, till the solution turned orange-red in colour. The excess of chlorine was then removed by a current of dry carbon dioxide. The clear solution was preserved in a bottle from which samples could be removed without contamination with the atmospheric moisture. The selenium content of the solution was estimated by the method suggested by McCullough[11] while the chlorine was determined by shaking the solution with potassium iodide and estimating the liberated iodine (by the thiosulphate method). Selenium chloride and potassium iodide had been found to react quantitatively yielding (in presence of light) potassium chloride, selenium and iodine. The selenium chloride solution had $56{\cdot}0 \times 10^{-6}$ g. atom of selenium per g. while the chlorine content was $55{\cdot}6 \times 10^{-6}$ g. atom per g. of stock solution. This showed that the selenium chloride was quite pure.

Reaction between potassium iodide and selenium chloride.—The estimation of iodine liberated by the decomposition of the selenium iodide constituted an easy method of determining the extent of reaction between potassium iodide and selenium chloride. The reaction between the two substances was very rapid at low temperatures. Thus, at $-10°$ C. the mixture of potassium iodide and selenium chloride solution had to be shaken for a period of only two minutes for the reaction to be complete. At the laboratory temperature (25° C.) however, the mixture had to be shaken for a much longer period (10–15 minutes) before the reaction could be complete. This result was unexpected since the reaction between thionyl chloride and potassium idoide (in the preparation of thionyl iodide[13]) was accelerated by a temperature increase. Further investigations revealed that at higher temperatures, the selenium and iodine (formed during the reaction) were strongly adsorbed by the potassium iodide, and reduced the effective area of the solid. This probably accounted for the retardation of the reaction at the higher temperature.

Hydrolysis of selenium iodide.—Selenium iodide might be expected to react with water in a way analogous to that of selenium chloride with water. On hydrolysis with water, selenium chloride produces selenium, selenious acid and hydrogen chloride. Hence selenium iodide could be expected to react with water yielding selenium, selenious acid and hydrogen iodide. As in the case of sulphur iodide,[12] a portion of the selenium iodide (being highly unstable) might also decompose into selenium and iodine. In experiments on the hydrolysis of selenium iodide, alkali cannot be used (*cf.* sulphur

iodide[12]) since selenium itself reacts with alkali[15] producing the selenide which then gets oxidised by the iodine. Even in neutral solutions, iodine oxidises selenium to selenious acid.[16] Thus when a solution of iodine (0·1 N) in carbon tetrachloride saturated with red selenium is shaken up with water for a period of one hour, the iodine consumed in oxidising the selenium amounts to about 7–8%. It is therefore necessary to conduct a blank experiment in order to determine the amount of iodine consumed in the oxidation of selenium. The following method was adopted to find out the extent of hydrolysis of selenium iodide. Precipitated cadmium carbonate was employed to neutralise the hydrogen iodide liberated during the reaction. Such neutralization was found necessary to avoid the reduction of selenious acid by hydrogen iodide.

A weighed quantity of the stock solution of selenium chloride (2–3 g.) was diluted with carbon tetrachloride (400 g.) and cooled to $-14°$ C. in a freezing mixture. The solution was then shaken up (in the dark) with dry potassium iodide (3–4 g.) for a period of one minute using a shaking machine. The clear liquid was divided into two portions; one portion was immediately shaken up with cadmium carbonate suspension in water for 15 minutes. The other was kept in sunlight to effect complete decomposition of the iodide; the solution was then treated with the aqueous suspension of cadmium carbonate under similar conditions of temperature and shaking. The iodine liberated in both cases was estimated as outlined above. The results are given in Table I.

TABLE I

Hydrolysis of selenium iodide by water in presence of cadmium carbonate

Period of shaking A	Iodine got by immediate shaking (g. atom of I per g. solution) B	Iodine got by shaking the mixture after exposure to light (g. atom of I per g. solution) C	$\frac{\text{Iodine in B}}{\text{Iodine in C}}$ D
1. 15 min.	$15{\cdot}8\times 10^{-8}$	$18{\cdot}1\times 10^{-8}$	0·87
2. 30 ,,	$12{\cdot}2\times 10^{-8}$	$14{\cdot}4\times 10^{-8}$	0·85
3. 30 ,,	$7{\cdot}1\times 10^{-8}$	$8{\cdot}5\times 10^{-8}$	0·84

The results indicate that the iodine content of the solution decomposed by light is always greater. When selenium iodide is shaken up with water the

reactions that take place are (1) decomposition and (2) hydrolysis, and can be represented as

(1) $Se_2I_2 \rightarrow 2\,Se + I_2$ (A) (Decomposition)

(2) $2\,Se_2I_2 + 3\,H_2O \rightarrow 3\,Se + H_2SeO_3 + 4\,HI$ (B) (Hydrolysis).

When the fresh solution is shaken up with water, a portion of the selenium iodide reacts according to (B), thus reducing the iodine content. But when the solution is exposed to light, the selenium iodide completely decomposes into the elements according to (A). Since no hydrolysis can take place in this case, the iodine content is larger by about 10–15%. In other words, about 10–15% of the selenium iodide hydrolyses with water while the rest merely decomposes. A similar result is also obtained in the hydrolysis of thionyl iodide[13] in presence of cadmium carbonate where only 3–4% hydrolyses, the rest getting decomposed. It can therefore be concluded that the carbon tetrachloride solution that has not been exposed to light, does contain selenium iodide, a portion of which hydrolyses on shaking with water.

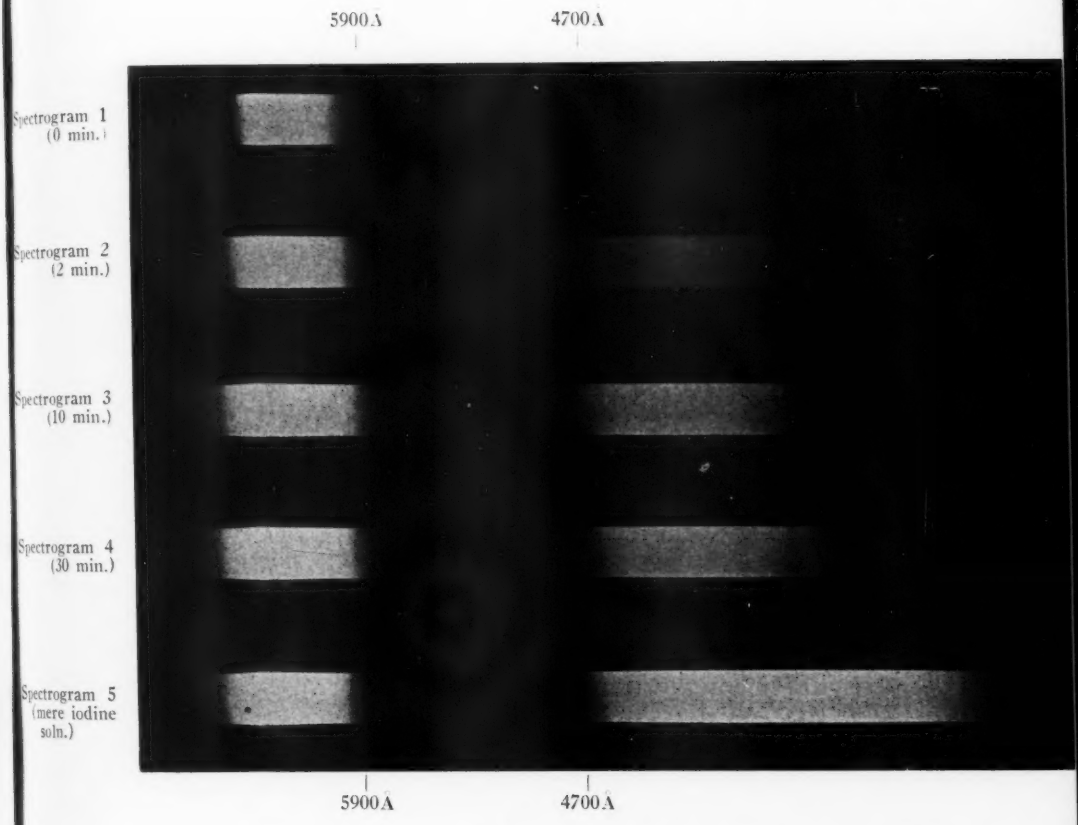
Absorption Spectrum Studies on Selenium Iodide.—The decomposition of selenium iodide can conveniently be followed up by a study of absorption spectra. A Hilger constant-deviation spectrograph was used in the investigations. The intensity of illumination was maintained uniform by passing a constant current through a tungsten filament lamp. The light was rendered parallel and passed through a quartz Baly tube filled with the selenium iodide solution prepared as outlined above. Since selenium iodide is highly photosensitive care has to be taken to avoid unnecessary exposure of the solution to light. Spectrogram 1 was taken with the fresh selenium iodide solution. The period of exposure was 15 seconds in each case. Even during this short interval of exposure to light, perceptible quantities of the selenium iodide were found to decompose. After the first exposure, the solution in the Baly tube was kept illuminated to effect the decomposition of the selenium iodide. Spectrograms 2, 3 and 4 were taken at intervals of 2, 10 and 30 minutes respectively. The last spectrogram is the absorption spectrum taken with a solution of pure iodine in carbon tetrachloride having the same iodine concentration as the decomposed selenium iodide solution.

The following information can be gathered by a study of the absorption spectra. When the selenium iodide solution is fresh (Spectrogram 1) there is practically complete absorption for all wave lengths below 5900 Å. But as the decomposition proceeds, the solution becomes more and more transparent in the violet region. Thus the transmission in the violet region is quite intense in spectrogram 2 and is at its maximum in the spectrograms

3 and 4. This shows that when the solution is exposed to the action of light for 2 minutes, only small quantities of the selenium iodide are left undecomposed. The similarity of spectrograms 3 and 4 indicates that the decomposition of selenium iodide is complete when the solution is exposed to light for a period of 10 minutes. It is of interest to note that light absorption by iodine is markedly affected by the presence of selenium in solution. A comparison of the spectrogram 4 (for a mixture of selenium and iodine in carbon tetrachloride, *i.e.*, the selenium iodide solution after complete decomposition) with spectrogram 5 (for pure iodine in carbon tetrachloride) shows that the absorption in the violet region is increased by the presence of selenium although a solution of selenium itself shows no absorption in this region. As will be pointed out later, this difference in absorption is assumed by McCullough[11] to be due to the formation of selenium iodide.

Discussion

The chemical and the spectroscopic evidence presented in this paper shows beyond doubt, that selenium iodide is formed when a dilute solution of selenium chloride is shaken up with dry potassium iodide. The iodide thus produced decomposes very rapidly in presence of light. The colour change when selenium is added to a solution of iodine in carbon tetrachloride (*cf.* Spectrograms 4 and 5) and the increase in solubility of selenium in carbon tetrachloride containing iodine, have been pointed out by McCullough[11] as evidence for the formation of selenium iodide in carbon tetrachloride solutions. The colour change might either be due to the formation of a definite compound, *viz.*, selenium iodide or due to the formation of a loose additive product between selenium and iodine. Iodine is known to form such additive products with alcohol, acetone and other liquids[17,18] in which it dissolves, giving a brown colour. The freezing point experiments also[18] confirm this view. Beckmann and Faust[19] tried similar cryoscopic experiments but could not obtain any evidence for the formation of a compound when selenium and iodine were dissolved in methylene iodide. The increase in solubility of selenium (brought about by the addition of iodine) in carbon tetrachloride cannot be taken as definite evidence in favour of the formation of selenium iodide. For, Amadori[20] has found that the solubility of sulphur in benzene and in other liquids is considerably increased by the presence of iodine, although it is definitely established that no sulphur iodide is produced when the two elements are dissolved in common solvents. In view of the high instability of selenium iodide in presence of light, it can be concluded that more experimental work is necessary before one can accept the view that selenium iodide is formed when the two elements are brought together in carbon tetrachloride solution.



Absorption Spectrum of Selenium Iodide solution in carbon tetrachloride

Summary

(1) Selenium monoiodide has been shown to be produced when a dilute solution of selenium chloride in carbon tetrachloride, is shaken with dry potassium iodide.

(2) The iodide is highly unstable in presence of light and decomposes into selenium and iodine.

(3) Hydrolysis of selenium iodide by water has been investigated.

(4) Decomposition of selenium iodide has been studied spectroscopically.

(5) The significance of the colour change brought about by the addition of selenium to a solution of iodine in carbon tetrachloride is discussed.

Acknowledgment

The author takes this opportunity to express his sincere thanks to Professor B. Sanjiva Rao for his keen interest in the work.

REFERENCES

1. Berzelius .. *Acad. Handl. Stockhol.*, 1818, **39**, 13.
2. Schneider .. *Pogg. Ann.*, 1866, **129**, 627.
3. Guyot .. *Compt. Rend.*, 1871, **72**, 682.
4. Pellini and Pedrina .. *Atti. Acad. Lincei.*, 1908, (5), **17**, (ii), 78.
5. Olivari .. *Ibid.*, 1908, (5), **17**, (ii), 566.
6. Beckmann and Hanslian .. *Z. anorg. Chem.*, 1913, **80**, 221.
7. ——— and Sitzb .. *Kgl. preuss. Akad.*, 1913, 886.
8. ——— and Grunthal .. *Z. anorg. Chem.*, 1914, **84**, 97.
9. ——————— .. *Ibid.*, 1918, **102**, 215.
10. Wright .. *J. Chem. Soc.*, 1915, **107**, 1527.
11. McCullough .. *J. Amer. Chem. Soc.*, 1939, **61**, 3401.
12. M. R. A. Rao .. *Proc. Ind. Acad. Sci.*, 1940, **11**, 162.
13. ——————— .. *Ibid.*, 1940, **11**, 185.
14. Lenher .. *J. Amer. Chem. Soc.*, 1920, **42**, 2498.
15. Tschugaev and Chlopin .. *Ber.*, 1914, **47**, 1269.
    ——————— .. *J. Russ. Phys. Chem. Soc.*, 1915, **47**, 364.
16. Engelhardt .. *Kolloid Z.*, 1928, **45**, 42.
17. Ley and Engelhardt .. *Z. anorg. Chem.*, 1911, **72**, 55.
18. Hildebr and and Glascock .. *J. Amer. Chem. Soc.*, 1909, **31**, 26.
19. Beckmann and Faust .. *Z. anorg. Chem.*, 1914, **84**, 103.
20. Amadori .. *Gazz. Chim. Ital.*, 1922, **52**, (1), 387.

RAMAN SPECTRA OF SOME ESTERS OF DI-CARBOXYLIC ACIDS

Oxalyl Chloride, Ethyl- and Methyl-Oxalate, Ethyl Malonate, Ethyl Phthalate, Ethyl Fumerate, Ethyl Maleate and Oxalic Acid

By Bishambhar Dayal Saksena

(From the Department of Physics, Indian Institute of Science, Bangalore)

Received October 8, 1940

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. Introduction

In the present paper a detailed analysis of the Raman Spectra of oxalic acid, oxalyl chloride and esters of some dicarboxylic acids has been undertaken. It includes an experimental study of the spectra and the polarisation characters of the lines. These substances present the problem of free rotation about the C–C bond and so, there is the possibility of a *cis* and a *trans* isomer in each case. The *trans* configuration possesses a centre of symmetry while the *cis* form does not. The lines which are forbidden in the former being antisymmetric to the centre, would appear in the latter and therefore, the Raman spectrum provides important evidence in favour or against the hypothesis.

2. Results

The results of the investigation are given in the following tables. The polarisation measurements for all the substances have been made for the first time. The state of polarisation is indicated by letters P and D—P, polarised, D, depolarised.

TABLE I

Oxalyl chloride			Ethyl oxalate		Methyl oxalate		
Kohlrausch	Author		Author		Author	Author	
Raman frequencies	Raman frequencies	Polarisation	Raman frequencies	Polarisation	(solid) Raman frequencies	(molten) Raman frequencies	(molten) Polarisation
188 (7)	184 (3)	P	325 (4)	P		180 (0)	D
266	..	..	390 (1)	P		380 (2)	P
274 (6)	272 (6)	P	867 (2) *s*	P		400 (3)	P
351 (1)	352 (0)	D	875 (5)	P	869 (9)	856 (12)	P
453 (6) *b* }	450–500 (5)	P	908 (0)	D	995 (6)	991 (5)	P
502 (5) }	(Very broad) band)		1019 (3)	D	1103 (0)	999 (2)	P
528 (3)	534 (2)	P	1105 (2) *s*	P	1189 (2) *s*	1190 (2)	P?
616 (12) *br*	619 (12) *br*	P	1293 (1)	..	1340 (6) *s*	1327 (2)	P
..	696 (0)	..	1399 (1)	D?		1385 (1)	D
1077 (4) *br*	1078 (3)	P	1456 (7)	D	1440 (5) 1445 (1)	1445 (8) double	D
1772 ± 10 (8)	1777 (8)	D	1756 (6) *br*	P	1757 (3)	1768 (12)	P
			2877 (1)	..	2858 (6)	2853 (6)	P
			2942 (8)	P	2963 (15) *br*	2962 (12)	P
			2983 (10)	D	3022 (3)	3017 (2)	P?
					3050 (4)	3049 (2) *br*	D

Oxalyl Chloride.—This has been investigated by Kohlrausch and Pongratz (1934) and Thatte and Joglekar (1937). The results of the latter are very incomplete. The frequency 266 reported by Kohlrausch has not been observed here, but a weak line at 696 is recorded.

Ethyl Oxalate.—References: Thatte and Ganesan (1931) and Kohlarusch and Pongratz (1933). The results reported are in agreement with those of Kohlrausch and Pongratz. The frequency 868 reported by the latter is a double line having frequencies 867 and 875.

Methyl Oxalate.—Reference: Kohlrausch and Pongratz (1933). The spectrum of the solid was taken by the method of complementary filters. The results for the molten state are in good agreement with those of Kohlrausch. The line 301 (½) reported by the latter appears to be *m* (25592)— 2961.

TABLE II

Ethyl malonate		Ethyl phthalate		Ethyl maleate		Ethyl fumerate	
Raman frequency	Polarisation	Raman frequency	Polarisation	Raman frequency	Polarisation	Raman frequency	Polarisation
		80 (1)				160 (2)	D
295 (0)				250 (0)		191 (2)	D
		128 (1) *br*	D			250 (2)	P
342 (3)	P						
		178 (1) *br*	D	382 (0)	D		
380 (3)	P						
		238 (1)		484 (1)	P?		
433 (0)	..					660 (0) ?	
		347 (2) *br*	P	594 (1)			
453 (0)		403 (2) *s*	P	865 (4)	P (·53)	865 (4)	P (·60)
568 (1)		528 (0)	P	975 (2)	D	893 (4)	D (·74)
608 (0)	P	548 (0) ?	?			978 (0)	P
676 (5)	D	648 (5)	P	1029 (2)	D (·70)	1031 (2)	D
789 (0) ?		785 (1)	..	1117 (3)	P	1117 (3)	P
847 (5)	P	843 (5)	P	1166 (3)	P	1169 (3)	P
869 (3)	P	863 (0)		1209 (2)		1214 (5)	P (·60)
934 (3)	P	1017 (2)	D				
				1291 (2)	P	1273 (1)	P?
962 (4)	P	1042 (10) *s*	P				
1034 (3)	D	1114 (2)	P	1358 (0)		1300 (2) *br*	P (·63)
1096 (1)	..	1166 (3)	P	1396 (1)	P	1370 (1)	P
1115 (4)	P	1275 (4)	P	1452 (5)	D (·78)	1456 (5)	D (·75)
1163 (2)	P	1300 (1)		1648 (8)	P (·55)	1640 (3)	P (·55)
		1370 (1)	P			1658 (10)	P (·45)
1274 (1)	P			1728 (10)	P (·47)		
		1396 (1)	P			1727 (12)	P (·41)
1297 (1)	P	1449 (4)	D	2932 (7)	P (·39)	2934 (6)	P (40)
1371 (2)	P	1487 (2)	P	2976 (6)	D	2982 (4)	D
1403 (1)	..	1577 (3)	P	3056 (4)	P	3060 (4)	P
1418 (2)	P	1602 (10) *s*	D				
1456 (8)	D	1726 (6)	P				
1752 (7) *br*	P	2880 (1)					
		2902 (2)	P				
2876 (3)	P						
		2943 (7)	P				
2941 (10)	P	2971 (2)	D				
2982 (12) *br*	D	3076 (8)	P				

Ethyl Malonate.—Reference: Ghosh and Kar (1931) and Kohlrausch, Pongratz and Seka (1933).

The results are in good agreement with previous workers. The frequency 368 reported by these workers is observed to be double. δ (C–H) frequency is also double.

Ethyl Phthalate.—References: Pongratz and Seka (1936), Bonino-Ansidei (1934), Matsuno and Han (1934) and Kohlrausch and Pongratz (1933).

Three low frequency lines are being reported for the first time.

Ethyl Maleate and Ethyl Fumerate—References: Hibben (1937), and Dadieu, Kohlrausch and Pongratz (1932).

The results obtained, in general, agree with those of the above workers. In ethyl fumerate, Kohlrausch and Pongratz report two frequencies 1640 (4), 1657 (8), while Hibben reports only one at 1656 (9). Author's results confirm those of Kohlrausch and Pongratz.

3. *Calculation of frequencies in Oxalic acid and Oxalyl chloride*

Both oxalic acid and oxalyl chloride belong to the type $A_2\,B_2\,C_2$ (*trans*) which has twelve normal modes. Six of these are Raman active, five being polarised and one depolarised. These five frequencies are planar frequencies and can be calculated by writing the potential and kinetic energies for totally symmetric vibrations. Using a potential function given by

$$2V = k(\Delta R)^2 + 2k_1(\Delta\gamma_1)^2 + 2k_2(\Delta\gamma_2)^2 + 2k_3\gamma_1^2(\Delta\alpha)^2 + 2k_4\gamma_2^2(\Delta\beta)^2$$

where k, k_1, k_2, k_3 and k_4 are the force constants of C–C, C = O, C – O, bonds and of C–C$\overset{O}{\diagdown\!\!\diagdown}$ and C-C$\overset{O}{\diagup}$ deformations respectively. We get the following secular determinants :

$$\begin{vmatrix} A-\frac{k}{\lambda^2} & F & G & H & I \\ F & \left(2B-\frac{k_1}{\lambda^2}\right) & J & K & L \\ G & J & \left(2C-\frac{k_2}{\lambda^2}\right) & M & N \\ H & K & M & \left(2D-\frac{k_3\gamma_1^2}{\lambda^2}\right) & O \\ I & L & N & O & \left(2E-\frac{k_4\gamma_2^2}{\lambda^2}\right) \end{vmatrix} = 0$$

Where $A = \frac{1}{4}(m_1 + m_2 + m) - \frac{1}{2\rho}(m_1\gamma_1 \sin\alpha - m_2\gamma_2 \sin\beta)^2$

$$B = m_1 - \frac{1}{2\rho} m_1^2 R^2 \sin^2\alpha$$

$$C = m_2 - \frac{1}{2\rho} m_2^2 R^2 \sin^2\beta$$

$$D = m_1\gamma_1^2 - \frac{1}{2\rho} m_1^2 (2\gamma_1^2 + R\gamma_1 \cos\alpha)^2$$

$$E = m_2 r_2^2 - \frac{1}{2\rho} m_2^2 (2\gamma_2^2 + R\gamma_2 \cos\beta)^2$$

$$F = m_1 \cos\alpha - \frac{R}{\rho} m_1 \sin\alpha (m_1\gamma_1 \sin\alpha - m_2\gamma_2 \sin\beta)$$

$$G = m_2 \cos\beta - \frac{R}{\rho} m_2 \sin\beta (m_2\gamma_2 \sin\beta - m_1\gamma_1 \sin\alpha)$$

$$H = -m_1\gamma_1 \sin\alpha - \frac{m_1}{\rho}(2\gamma_1^2 + R\gamma_1 \cos\alpha)(m_1\gamma_1 \sin\alpha - m_2\gamma_2 \sin\beta)$$

$$I = -m_2\gamma_2 \sin\beta + \frac{m_2}{\rho}(2\gamma_2^2 + R\gamma_2 \cos\beta)(m_2\gamma_2 \sin\beta - m_1\gamma_1 \sin\alpha)$$

$$J = \frac{m_1 m_2}{\rho} R^2 \sin\alpha \sin\beta$$

$$K = -\frac{m_1^2}{\rho}(2\gamma_1^2 + R\gamma_1 \cos\alpha) R \sin\alpha$$

$$L = \frac{m_1 m_2}{\rho}(2\gamma_2^2 + R\gamma_2 \cos\beta) R \sin\alpha$$

$$M = \frac{m_1 m_2}{\rho}(2\gamma_1^2 + R\gamma_1 \cos\alpha) R \sin\beta$$

$$N = -\frac{m_2^2}{\rho}(2\gamma_2 + R\gamma_2 \cos\beta) R \sin\beta$$

$$O = \frac{m_1 m_2}{\rho}(2\gamma_1^2 + R\gamma_1 \cos\alpha)(2\gamma_2^2 + R\gamma_2 \cos\beta)$$

$$\rho = \tfrac{1}{2}(m + m_1 + m_2) R^2 + 2m_1(\gamma_1^2 + R\gamma_1 \cos\alpha) + 2m_2(\gamma_2^2 + R\gamma_2 \cos\beta)$$

and $\omega = \dfrac{\lambda}{2\pi C}$, ω being the frequency in cms.$^{-1}$ and C, the velocity of light.

According to the measurements of Robertson and Woodwards (1936) in oxalic acid $\gamma_{c-o} = 1{\cdot}3$, $\gamma_{c=o} = 1{\cdot}24$, $\gamma_{c-c} = 1{\cdot}43 \times 10^{-8}$ cms. C–C$\diagup\!\!\diagup^{O}$ $= 121°$, C–C$\diagup^{O}$ $= 126°$. Assuming that k (C – C) $= 4{\cdot}5$, $k_3 = k_4 = 0{\cdot}4 \times 10^5$ dynes, k_1 (C = O) $= 9{\cdot}16$, k_2 (C— O) $= 5{\cdot}84 \times 10^5$ dynes, we get the roots of the secular equation as 1741, 1439, 700, 449 and 201, the observed frequencies being 1746, 1462, 844, 465 and 248.

In oxalyl chloride C—C$\diagup\!\!\diagup^{O}$ $= 120°$, C—C$\diagup^{C}$ $= 109°\ 30'$ according to Wierl (1930); but the other distances are not known. We take these as follows: C—Cl $= 1{\cdot}74 \times 10^{-8}$ (C—Cl distance in ethylene halides), (C = O) $= 1{\cdot}24 \times 10^{-8}$ cms. (C = O distance in oxalic acid), C–C $= 1{\cdot}43 \times 10^{-8}$ (C–C distance in oxalic acid) k_2 (C–Cl) force constant $= 2{\cdot}2 \times 10^5$ dynes [van

Vleck's (1933) value in ethyl chloride], $k_3\left(\text{C–C}\diagup\!\!\!\diagup\text{O}\right) = 0{\cdot}22$ (van Vleck's value), $k_4\left(\text{C–C}\diagup\!\!\!\diagup\text{O}\right) = 0{\cdot}4 \times 10^5$ dynes, k (C–C) $= 4{\cdot}5 \times 10^5$ and k_1 (C = O) $= 11{\cdot}2 \times 10^5$ dynes. The distances given above are approximate but cannot be far from the correct values. The secular determinant gives the following frequencies: 1785, 1082, 548, 270 and 140; the observed values being 1777, 1078, 619, 272 and 182.

These calculations are only approximate; but they show what frequencies can be assumed as fundamentals and what is the nature of vibration of the given frequency. The observed frequencies in oxalic acid and oxalyl chloride can be arranged according to their modes of vibration which we denote by ω. We have

ω_1	ω_2	ω_3	ω_4	ω_5	ω_6	
1746	1462	844	465	248	1368	in oxalic acid
1777	619	1078	272	182	450–500	in oxalyl chloride

ω_1 is an antisymmetric oscillation of group $\left(\text{C}\begin{smallmatrix}\nearrow\text{O}\\ \searrow\text{O}\end{smallmatrix}\right)$, ω_2 is the symmetric oscillation of this group, ω_3 is the C–C oscillation, ω_4 and ω_5 are deformation oscillations, and ω_6 is a depolarised perpendicular vibration (not calculated).

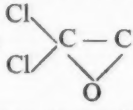
3. *Discussion*

Oxalic Acid.—The Raman frequencies in oxalic acid are given below:

Crystal			Solution				
A	H	A. L	Rao	H	A. L	G	Mean
			248	395 (*m*)			248
485		485	480	453 (*m*)	493	450 (2)	465 (2)
			673 ?				
854 (6)	847	854	845 (s)	842 (5)		847 (4)	844 (5)
1360 ($\frac{1}{2}$)	1365	..		1310 (ω)	1375	1372 ($\frac{1}{2}$)	1368 ($\frac{1}{2}$)
1486 (2)	1470	1471	1430 ± 30	1460 (*d*)		1459 (1)	1462 (1)
..	..	1661	1656	1645	1647	1631 (2)	1648 (2)
		1759	1744 (3)	1740 (*m*)	1749	1740 (4)	1740 (4)

A—Ananthakrishnan (1937), H—Hibben (1937), A. L—Angus, Leckie (1936), G—Gupta (1936)

Oxalic acid shows only seven lines of which five have been accounted for on the basis of the *trans* symmetry. Of the remaining lines, 1368 ($\frac{1}{2}$) and 1648, the first one is the depolarised perpendicular type of vibration ω_6. This line appears depolarised in both methyl and ethyl oxalates. The other represents the carbonyl frequency of the ionised molecule, and it occurs in solution as is apparent from the results given above. It appears, therefore, that oxalic acid possesses a *trans* symmetry.

Oxalyl Chloride.—The Raman lines 184, 272, 619, 1078 and 1777 have already been assigned as fundamental frequencies. The remaining lines observed are 352, 450–500 (br), 534 and 696. The broad frequency 450–500 is most likely the fundamental frequency ω_6. All the lines 184, 272, 619, 1078 and 1777 should be polarised and 450 depolarised. Polarisation results however, show that 1777 is depolarised while 450 (br) is polarised, and both the lines 534 and 352 are polarised. The latter frequencies cannot be classified as overtones, because the lines are fairly strong and the differences between the given frequencies and the first overtones of 272 and 184 cms.$^{-1}$ are rather large, *viz.*, 10 cms.$^{-1}$ in the first case and 16 cms.$^{-1}$ in the second case. To account for the presence of these extra lines and also for the anomalous polarisation of the lines 1770 and 450–500 there are three possibilities: (1) the molecule possesses an unsymmetrical form, (2) the molecule has a *cis* form and (3) there is a small rotation of the molecule about the stable *trans* form. In the unsymmetrical form  suggested by Heinberger, Maiyer and Froschl (1932) the Raman lines will all be partially polarised and there will be no depolarised line in the spectrum. Further, the strong frequencies 808, 869, and 1100 characteristic of ethylene oxide ring should be present (Ananthakrishnan, 1937). The spectrum shows only one strong frequency at 619 and one depolarised line. Thus the polarisation behaviour as well as the Raman spectrum does not favour the unsymmetrical form. In the *cis* form there should be five polarised and seven depolarised lines. The *cis* form will explain the depolarised behaviour of the line 1770, because this vibration now becomes antisymmetric to the elements of symmetry; but the large number of depolarised lines (seven) needed for the *cis* form makes this assignment improbable. The third assumption appears to be the most acceptable. The small oscillation about the *trans* form explains why the lines in the spectrum are in general broad and secondly, it will also explain the observed depolarisation of the line 1770 and the polarisation of

line 450, on account of a disturbance of symmetry. The observed lines 534, 696 and 352 may represent the antisymmetric vibrations of the *trans* configuration which come out with feeble intensity on account of this oscillation. This hypothesis will also explain the small dipole moment of 0·92 D observed by Martin and Partington (1936).

Methyl Oxalate.—If the molecule exists in a *trans* state, the symmetry of the molecule will be C_{2h}, the two hydrogen atoms of the methyl radical being symmetrical with respect to the plane of the molecule. The number of infra-red and Raman lines to be expected is given in the following table:

C_{2h}	Whole molecule	Core only barring H atoms	C-H frequencies	Selection rules	
				Raman	Infra-red
A_g	12	7	5	Pol.	*f*
B_u	7	3	4	*f*	*a*
A_u	6	2	4	Dep.	*f*
B_g	11	6	5	*f*	*a*

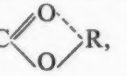
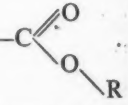
The Raman spectrum of methyl oxalate in the region below 1800 shows 8 polarised and 2 depolarised lines besides the (C–H) frequency at 1445. The lines 999 (6) and 991 (6) which represent a splitting of the C–O oscillation are due to the coupling of adjacent C–O bonds. The seven polarised lines are 1768, 1327, 1190, 991, 856, 400 and 380 and the two depolarised lines are 1385 and 180 ?. In the C–H region there should be five polarised and four depolarised lines. According to Reitz and Sabathy (1938) the vibrations of a methoxy group (OCH_3) are $\omega_{3,5}$, ω', ω'' and $\omega_{2,4}$; $\omega_{2,4}$ and $\omega_{3,5}$ being degenerate frequencies. In methyl oxalate the symmetry of the group is reduced from C_{3v} to C_{2h} and so the degenerate vibration $\omega_{3,5}$ is replaced by a doublet at 1445, and the two lines 3017 and 3049 represent ω_2 and ω_4. On account of the removal of degeneracy, one of the two lines ω_2 and ω_4 will be polarised and the other depolarised. The broad line 3049 is depolarised, and 3017 is polarised. ω' and ω'' may be identified with the lines 2853 and 2962, both of which are polarised.

In passing from the solid to the liquid state, the Raman spectrum of methyl oxalate shows the following changes in both frequency and intensity.

Liquid ..	3017 (2)	2853 (6)	*i*—1768 (12)	1327 (2)	1001 (2)	991 (5)	855 (10)
Solid ..	3022 (3)	2858 (6)	*i*—1757 (3)	1340 (6) *s*	..	995 (6)	869 (9)

The lines in the liquid are generally broad and diffuse; the changes in the breadth of the lines 3017 and 3049 is very pronounced. The significant changes in intensity occur in the lines 1327 and 1768 of the liquid and appreciable frequency shifts occur in the lines 1768, 1327 and 855 of the liquid. These lines may be identified as the vibration frequencies of the group $\left[C-C\begin{matrix}O\\O\end{matrix}\right]$; the line 1768 represents an asymmetric oscillation of the carboxyl, 1327 represents a symmetric oscillation of the same and 855 is the C–C oscillation. During the process of heating the changes that occur are such that the C = O force in the liquid is greater than that in the solid. This also changes the other frequencies of $C-C\begin{matrix}O\\O\end{matrix}$ group. It is seen from the calculations in oxalic acid that when the C = O force is increased, both ω_2 and ω_3 are diminished whereas ω_1 is increased as shown below:

k_1	ω_1	ω_2	ω_3
9·2	1741	1439	700
10·0	1780	1380	685

This is actually observed on heating methyl oxalate; both the lines 1340 and 869 of solid are diminished in frequency. We may, therefore, conclude that the changes observed on heating methyl oxalate are due to an increase in the C = O force. This is readily understood if we assume that in the solid state the methyl group exists in the *cis* position  , where R represents the methyl group, and on melting it changes over to  .

This is also otherwise evident because in the solid state, there must be a greater bonding between the hydrogens of the methyl group and the free oxygen of the carboxyl, tending to reduce the C = O force. In the *trans* form ω_4 and ω_5 are forbidden while ω_1 and ω_3 are polarised. The observed lines in the above table have been assigned to the various frequencies with due regard to their polarisation characters.

General Remarks.—A study of the spectra shows that some lines appear with nearly the same frequency and state of polarisation in all the compounds containing the ethoxy group C_2H_4O. Considering this as a triatomic molecule consisting of CH_3, CH_2 and O and knowing the frequencies ω_1, ω_2 and

ω_3 characteristic of this group in different substances, we can find the force constants f_1, f_2 and d of the C–O and C–C bonds and of the C–C$\diagup\!\!\diagdown^{O}$ deformation respectively in different substances studied.

	ω_2 (p)	ω_1 (p)	ω_3 (D)	d	f_2	f_1
Ethyl oxalate ..	390 (1)	875 (5)	1019 (3)	0·41	3·39	4·05
Ethyl malonate ..	342 (3)	847 (5)	1034 (3)	0·302	3·39	4·07
Ethyl phthalate ..	347 (2)	843 (5)	1017 (2)	0·312	3·37	3·91
Ethyl maleate ..	382 (0)	865 (4)	1029 (2)	0·39	3·39	4·08
Ethyl fumerate ..	384 (0)	865 (4)	1031 (2)	0·39	3·40	4·09
Ethyl alcohol .	433 (1)	883 (6)	1051 (3)	0·52	3·6	4·1

It is seen that in all the compounds studied the C–C force constant is 3·39 and the C–O force constant 4·05.

In conclusion the author wishes to express his thanks to Sir. C. V. Raman for his kind interest in the work.

Summary

The Raman spectra of oxalic acid, ethyl and methyl oxalates, oxalyl chloride, ethyl malonate, ethyl phthalate, ethyl maleate, and ethyl fumerate are studied and their state of polarisation determined. The fundamental frequencies of oxalic acid and oxalyl chloride have been calculated on the *trans* model. The Raman spectrum of oxalic acid shows satisfactory agreement with this model ; but the results of oxalyl chloride indicates an oscillation about the *trans* configuration. The spectrum of methyl oxalate shows striking changes while passing from the solid to the liquid state, which is probably due to a change in the C = O force, resulting from a change of the methyl group (R) from the form —C(=O)···O—R in the solid to —C(=O)—O—R in the liquid.

REFERENCES

1. Kohlrausch and Pongratz .. *Ber.*, 1934, **67**, 976.
2. Thatte and Joglekar .. *Phil. Mag.*, 1937, **23**, 1067.
3. ——— and Ganesan .. *Ibid.*, 1931, **12**, 823.
4. Kohlrausch and Pongratz .. *Ber.*, 1933, **66**, 1355.
5. Ghosh and Kar .. *Jour. Phys. Chem.*, 1931, **35**, 1735.

6. Kohlrausch, Pongratz and Seka .. *Ber.*, 1933, **66**, 1.
7. Pongratz and Seka .. *Wien. Ber.*, 1936, **144**, 439.
8. Bonino, Manzoni-Ansidei .. *Mem. Accad. Bologna*, 1934, Feb.-May.
9. Matsuno and Han .. *Bull. Chem. Soc., Japan*, 1934, **9**, 88.
10. Hibben .. *Jour. Chem. Phys.*, 1937, **5**, 786.
11. Dadieu, Kohlrausch and Pongratz *Monatsh*, 1932, **60**, 206.
12. Robertson and Woodwards .. *Jour. Chem. Soc.*, 1936, 1817.
13. Wierl .. *Phy. Zeit.*, 1930, **31**, 366.
14. Van Vleck .. *Jour. Chem. Phys.*, 1933, **1**, 350.
15. Heinberger, Maiyer and Froschl *Monatsh*, 1932, **59**, 256.
16. Ananthakrishnan .. *Proc. Ind. Acad. Sci.*, (A), 1937, **4**, 182.
17. Gupta .. *Ind. J. Phys.*, 1936, **10**, 199.
18. Angus and Leckie .. *J. Chem. Phys.*, 1936, **4**, 83.
19. Martin and Partington .. *Jour. Chem. Soc.*, 1936, 1178–82.
20. Reitz and Sabathy .. *Zeit. f. Phys. Chem.*, 1938, **41**, 158.

1485-40 Printed at The Bangalore Press, Bangalore City, by G. Srinivasa Rao, Superintendent and Published by The Indian Academy of Sciences, Bangalore

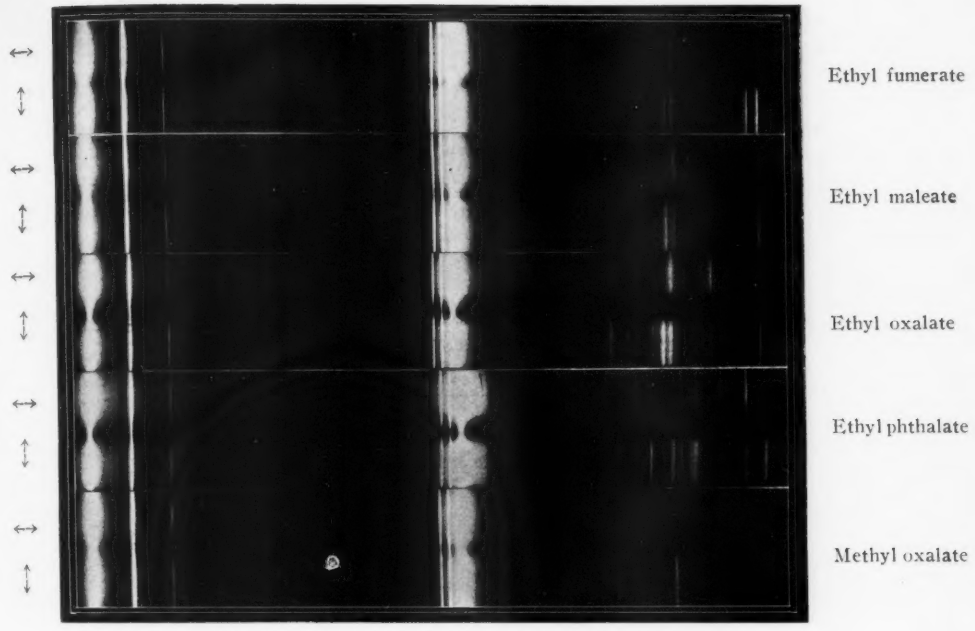


FIG. 1. State of polarisation of Raman lines

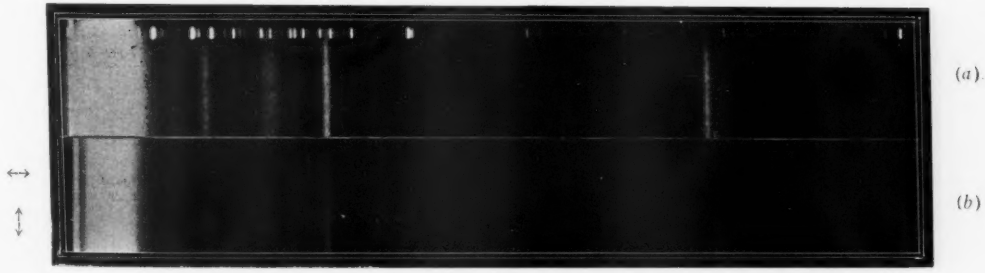


FIG. 2. (*a*) Raman spectrum and (*b*) State of polarisation of lines in oxalyl chloride

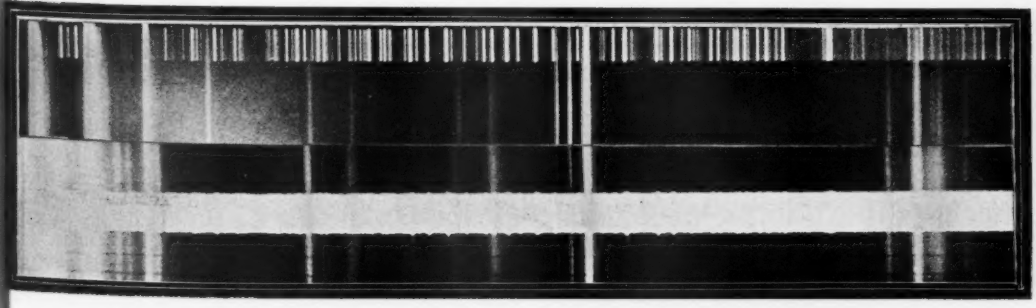


FIG. 3. Raman spectra of methyl oxalate: (*a*) Solid; (*b*) Liquid

ERRATA

Vol. XII, No. 3, September 1940

Page	Line				
324	2	*read*	Q'_z	*as*	Q'_2
324	4	,,	Q'_2	*as*	Q_z
326	2	,,	$\left\{12+\frac{16}{3}(1-\cos\phi)^2+16(1-\cos\phi)\right\}$		
		as	$\left\{12+\frac{16}{3}(1-\cos\phi)^2-16(1-\cos\phi)\right\}$		
326	17	,,	$\lambda_5^2=\frac{3}{2}\left(\frac{R_1+d_1}{m}\right)$		
		as	$\lambda_5^2=\frac{3}{2}\left(\frac{k_1+d_1}{m}\right)$		